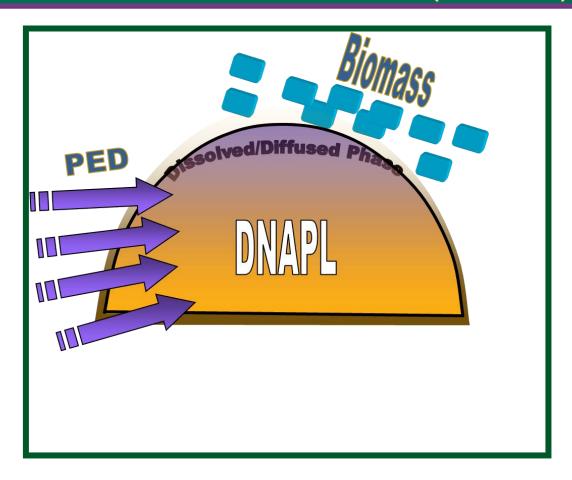
ESTCP Cost and Performance Report

(ER-200716)



Improving Effectiveness of Bioremediation at DNAPL Source Zone Sites by Applying Partitioning Electron Donors (PEDs)

July 2014

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ACRONYMS AND ABBREVIATIONS

1,1,1-TCA 1,1,1-trichloroethane

AFCEE Air Force Center for Engineering and the Environment

bgs below ground surface

CCAFS Cape Canaveral Air Force Station

cDCE cis-1,2-dichloroethene

CFC113 1,1,2-trichloro-1,2,2-trifluoroethane

CMS Corrective Measures Study

DEM/VAL demonstration/validation

Dhc Dehalococcoides ethenogenes

DHG dissolved hydrocarbon gas

DNAPL dense non aqueous phase liquid

DO dissolved oxygen DP direct push

DPT direct-push technology DQI data quality indicator

EISB enhanced in situ bioremediation ESB Engineering Support Building ESC Engineering Service Center

ESTCP Environmental Security Technology Certification Program

EVO emulsified vegetable oil

EXWC Expeditionary Warfare Center

ft feet

ft BLS feet below land surface

GAC granular activated carbon

gpm gallons per minute

GT Georgia Institute of Technology

IDW investigation derived waste IMWP Interim Measure Work Plan

ITRC Interstate Technology Regulatory Council

KBr potassium bromide

kg kilogram kgal kilogallons

KI potassium iodide KSC Kennedy Space Center

ACRONYMS AND ABBREVIATIONS (continued)

lb pound

LC34 Launch Complex 34

μg/L micrograms per liter

MCL maximum contaminant level
mg/kg milligram per kilogram
mg/L milligrams per liter
MIP membrane interface probe

MW monitoring well

NA not applicable

NAPL non-aqueous phase liquid

NASA National Aeronautics and Space Administration

NAVFAC Naval Facilities Engineering Command

NAVFACSW NAVFAC Southwest

nBA n-butyl acetate nBuOH n-Butanol

NFESC Naval Facilities Engineering Services Center

nHEX n-hexanol

NPV net present value

O&M operation and maintenance ORP oxidation reduction potential

PARCCS precision, accuracy, representativeness, comparability, completeness, &

sensitivity

PCE tetrachloroethene

PED partitioning electron donor psi pounds per square inch PVC polyvinyl chloride

QA quality assurance QC quality control

RCRA Resource Conservation and Recovery Act

RFI RCRA Facility Investigation

RW extraction well

TCE trichloroethene

TDP Technology Demonstration Plan

TOC total organic carbon

TVOC total volatile organic compounds

UIC underground injection control

ACRONYMS AND ABBREVIATIONS (continued)

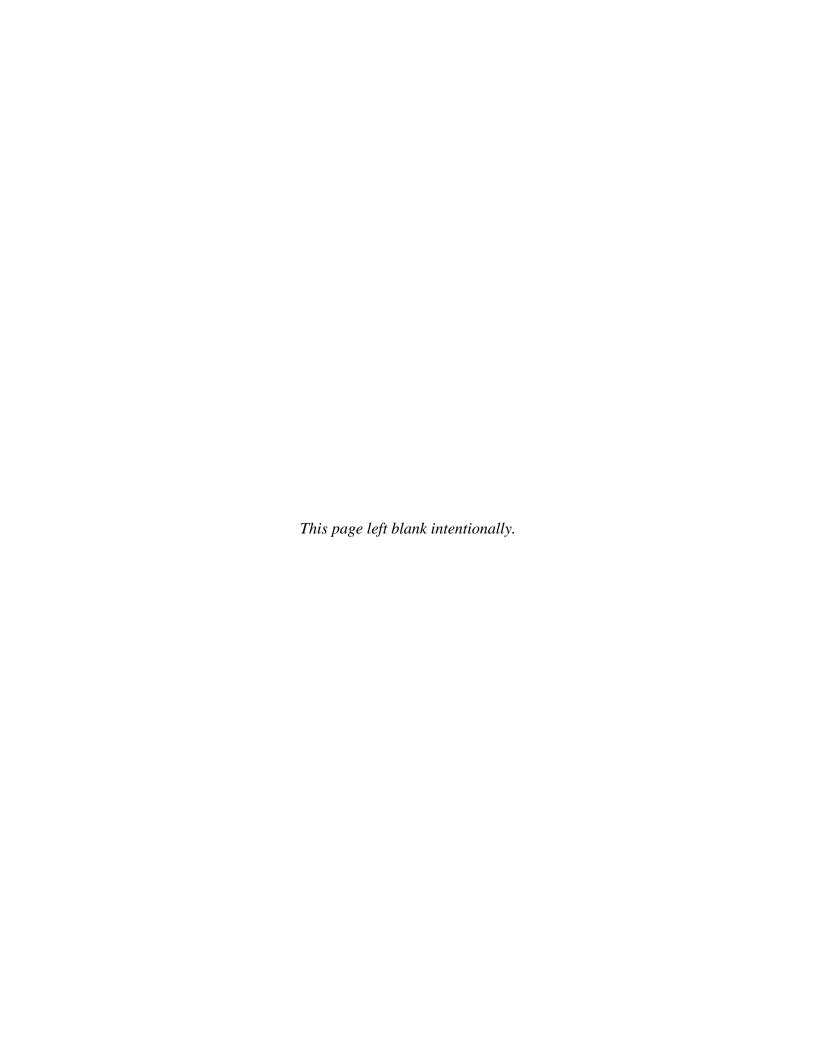
USEPA U.S. Environmental Protection Agency

VC vinyl chloride

vcrA vinyl chloride reductase enzyme

VFA volatile fatty acid VOC volatile organic carbon

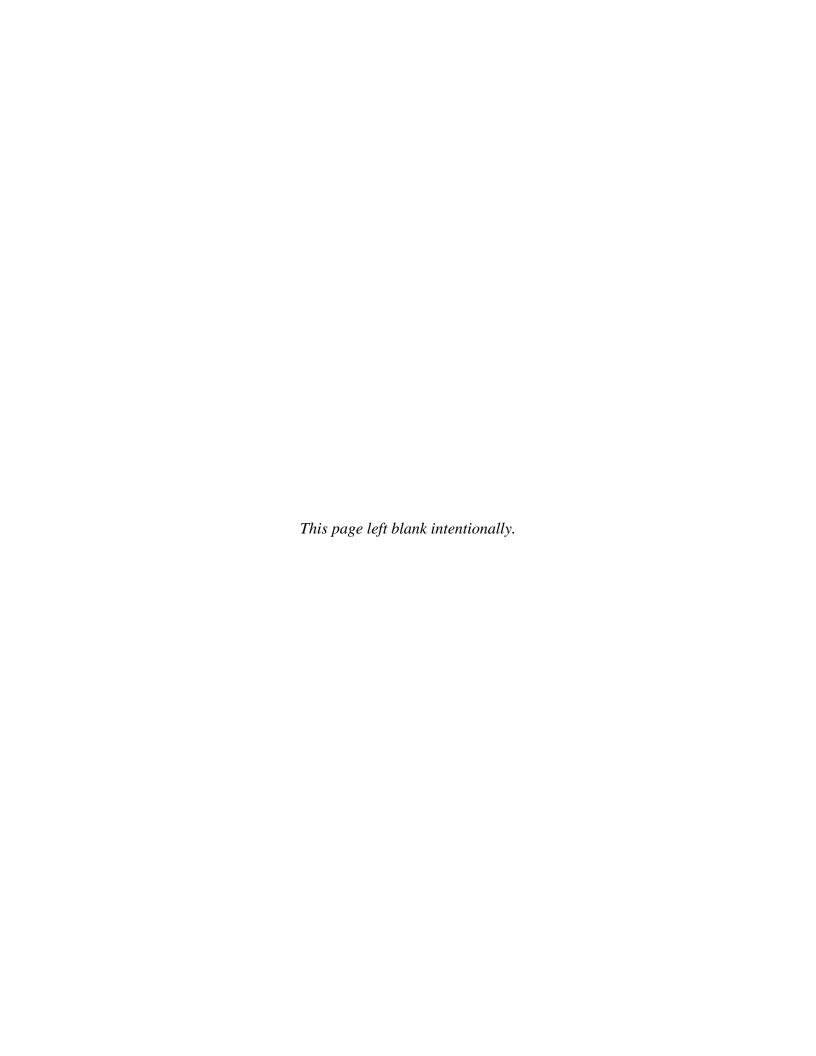
yd³ cubic yard



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Contact information for the key team members are provided in Appendix A.



EXECUTIVE SUMMARY

OBJECTIVES

Partitioning electron donors (PED) are electron donors that partition directly into a target dense non aqueous phase liquid (DNAPL). PEDs are water soluble, hence are easily transported to a DNAPL source zone. This property aids in their mixing throughout the source zone and maximizes contact with the DNAPL. Even at high dose rates, PEDs are slowly metabolized, which facilitates delivery without significant loss and allows efficient distribution throughout the source zone. The objectives of the field demonstration/validation (DEM/VAL) included: (1) Demonstrate application of the PED technology at field scale, assess the ability to distribute PED within the source area and enhance biodegradation; (2) Validate the enhanced performance and efficiency of DNAPL dissolution and dechlorination following the injection of a PED; and (3) Collect cost and performance data for the application of PEDs for source zone bioremediation.

TECHNICAL DESCRIPTION

Based on treatability studies to evaluate candidate PED (Caprio et al., 2011) n-butyl acetate was selected for the DEM/VAL. The technology field demonstration was conducted at a source zone (Hot Spot 1) at the National Aeronautics and Space Administration (NASA) Launch Complex 34 (LC34). At this site, trichloroethene (TCE) DNAPL is associated with a silty sand/silty clay horizon at about 42 to 48 feet below land surface (ft BLS) and TCE concentrations up to 141,000 micrograms per liter (μ g/L) had been reported.

Two sweep zones, one above and one below the clay horizon were separately instrumented and operated, providing two data sets with which to evaluate the performance of the PED technology. Each sweep zone was instrumented with a single central extraction well, from which integrated groundwater samples were collected routinely to monitor the average concentration of various dissolved constituents over time. Extracted groundwater was returned to the aquifer through a set of ten groundwater injection wells on the perimeter of the TCE plume. At each of five injection locations, a pair of injection wells was installed, above and below the clay horizon, to help create an inward hydraulic gradient and promote horizontal flow across the top and base of the clay horizon.

Routine groundwater samples were collected during recirculation to assess the concentrations and flux of various compounds. Comparison of concentrations (volatile organic compounds [VOC], PED, tracers) in groundwater initially and over time extracted from the central wells were used to assess the "disturbance effect" of direct injection and evaluate the quantity of n-Butyl acetate (nBA) that was taken up by the DNAPL. Soil sampling was conducted before (baseline delineation) and after the demonstration area was amended, to establish mass distribution within the plots, and again after operation was halted, to assess changes over the DEM/VAL operation and to correlate these results with the observed trends in groundwater concentrations.

DEMONSTRATION RESULTS

The PED was able to promote biodegradation and achieved sustained production of dechlorination products. Donor longevity was assessed and donor was present up to one year following PED injection. Tests confirmed that the PED was capable of partitioning into a TCE DNAPL.

The use of PEDs for source zone bioremediation is expected to be cost-equivalent to emulsified vegetable oil applications. Donor longevity of nBA was at least equivalent to emulsified vegetable oil applications for similar applications. Time-trend data for the electron donor concentrations was also monitored and compared. Results using nBA were compared to those from tests that used soluble donors, such as lactate; the nBA provided a longer period of activity, since it partitioned into residual non-aqueous phase liquid (NAPL) initially and then gradually became re-supplied to groundwater whereas any unused soluble donor would have migrated away from the NAPL source area.

IMPLEMENTATION ISSUES

As with other source application based technologies understanding and identifying the extent of the source zone (i.e., site characterization) to estimate the mass of DNAPL present should be completed. Such an effort would require capital cost expenditures but should reduce application costs. Another limitation of using the PED technology would include the pre-requisite of suitable geochemical conditions to promote biodegradation through reductive dechlorination.

Delivering the PED into the source area is critical. This project showed that the selected PED, nBA, can; (1) achieve high rates of biologically-enhanced DNAPL dissolution; (2) be easily and effectively delivered; and (3) sustain donor supply at an effective concentration at the DNAPL:water interface. The PED was water soluble, easily transported to a DNAPL source zone, and less expensive to deliver than other commercial products.

1.0 INTRODUCTION

1.1 BACKGROUND

Enhanced in situ bioremediation (EISB) can be a cost effective approach for remediation timelines at sites impacted with dense non aqueous phase liquids (DNAPL) such as trichloroethene (TCE) and tetrachloroethene (PCE). Compared to other remedial techniques, the estimated cost reported from McDade et al. (2005) for EISB was \$29 per cubic yard (yd³), in comparison to \$88 per yd³ for thermal treatment, \$125 per yd³ for chemical oxidation and \$385 per yd³ for surfactant enhanced removal, respectively. McDade et al. also indicated that the lower cost for in situ bioremediation was "related to the cheaper unit cost of enhanced bioremediation amendments (electron donor)." Vegetable oil, a low priced electron donor, costs approximately \$1.00 per pound (lb). Yet, although the purchasing cost is economical, the amount of electron donor applied at impacted sites greatly affects the cost and efficacy of conducting EISB. It has been demonstrated by Harkness (2000) that the cost of electron donor can represent up to 50% of the net present value (NPV) cost when applied using passive (i.e., biostimulation) methods.

To achieve high rates of biologically-enhanced DNAPL dissolution, electron donor needs to be delivered, as well as sustained at an effective concentration at the DNAPL:water interface for the growth of and consumption by dechlorinating biomass. In heterogeneous geological formations containing DNAPL pools and ganglia, there's uncertainty on the efficacy of aqueous and emulsified electron donors; i.e., will the electron donor be present at the DNAPL:water interface with a concentration appropriate to achieve maximum biodegradation rates and dissolution effects? As a result, typical electron donor applications use five to ten times the amount of electron donor required as a safety factor. This increases the application cost significantly.

Partitioning electron donors (PED) are electron donors that partition directly into a target DNAPL. PEDs are water soluble, hence are easily transported to a DNAPL source zone. This property aids in their mixing throughout the source zone and maximizes contact with the DNAPL. Additionally, PEDs partition strongly into DNAPL from which they are subsequently released, providing a high percentage of reducing equivalents that can be consumed in the reductive dechlorination process.

1.2 OBJECTIVES OF THE DEMONSTRATION

The objectives of this field demonstration/validation (DEM/VAL) were to:

- 1. Demonstrate application of the PED technology at field scale, assessing the ability to distribute PED within the source area and enhance biodegradation;
- 2. Validate the enhanced performance and efficiency of DNAPL dissolution and dechlorination following the injection of a PED; and
- 3. Collect cost and performance data for the application of PEDs for source zone bioremediation and provide reliable technical data relevant to field-scale implementation of the PED technology, including documentation of the expected reduction in duration and cost of remediation of DNAPL source sites.

The field DEM/VAL was conducted at the National Aeronautics and Space Administration (NASA) Launch Complex 34 (LC34), located on Cape Canaveral Air Force Station (CCAFS), Cape Canaveral, Florida. A TCE source area, designated as Hot Spot 1, was identified as separate and distinct from the volatile organic carbon (VOC) mass beneath the Engineering Support Building (ESB). This site had a TCE- non-aqueous phase liquid (NAPL) source that appeared primarily to exist within/near a lower conductivity unit. Site conditions were appropriate and a suitable on-site support network existed for execution of the DEM/VAL.

1.3 REGULATORY DRIVERS

The U.S. Environmental Protection Agency (USEPA) maximum contaminant level (MCL) for PCE and TCE in drinking water is 5 micrograms per liter (μ g/L). The MCLs for vinyl chloride (VC) and cis-1,2-dichloroethene (cDCE) are 2 μ g/L and 70 μ g/L, respectively. A significant number of sites have VOCs present as free phase DNAPLs that will act as long term sources of VOCs to groundwater.

2.0 TECHNOLOGY

The following sections provide an overview of the technology (Section 2.1) and a discussion of the potential advantages and limitations of the technology (Section 2.2).

2.1 TECHNOLOGY DESCRIPTION

PEDs are electron donors that partition directly into the DNAPL. The development of the PED approach is a combination of partitioning tracer and electron donor technologies. When PED encounters free phase DNAPL, it partitions into the DNAPL with a corresponding decrease in its aqueous phase concentration. Depending on the method of PED addition (e.g., a pre-determined mass of PED that is injected in batches, or a constant or stepped concentration delivery scheme), different breakthrough concentrations of PED at the extraction will be observed over time. Analysis of the breakthrough will indicate when the DNAPL in the source area has taken up sufficient PED to achieve the target loading. Eventually, the DNAPL-phase PED will partition back into the groundwater and provide a much higher and sustained concentration of electron donor at the DNAPL:water interface than is achieved with existing electron donor delivery methods. The outcome is the promotion of dechlorinating biomass growth close to the DNAPL, which results in sustained enhanced DNAPL dissolution rates. This approach increases the efficiency of electron donor use for two reasons: (1) it avoids loss (i.e., microbial consumption) of donor as it migrates towards the DNAPL; and (2) it reduces the consumption of electron donor in microbial processes not associated with reductive dechlorination.

As a precursor to the field DEM/VAL, laboratory treatability studies were conducted to evaluate two candidate PEDs, n-butyl acetate (nBA) and n-hexanol (nHEX). This work was performed primarily at the Georgia Institute of Technology (GT) and funded by Naval Facilities Engineering Command (NAVFAC) Southwest (NAVFACSW). These studies are described in Section 5 of this report. The results suggested that nBA would be a suitable PED for field deployment. In water, nBA undergoes hydrolysis to form acetate and n-butanol. The n-butanol can then be utilized by fermenting organisms to produce butanoate, acetate, and hydrogen. Results of these evaluations were presented in the Laboratory Treatability Study Report (NAVFAC Engineering Service Center [ESC] et al., 2010).

2.2 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

The main advantages of the PED technology over other treatment technologies include:

- Cost the selected PED material, n-butyl acetate, is generally inexpensive;
- Reduced risk of mobilization predictable impact on DNAPL density or viscosity to mitigate the potential effects on DNAPL mobilization; and
- Safety non-toxic or generally regarded as safe for use in food products.

The main limitations of using the PED technology are:

• Requires characterization – similar to any source remediation technology, understanding and identifying the extent of the source zone is required to estimate the

- DNAPL mass present and thereby, minimize the zone to be treated. Such an effort would require capital cost expenditures; and
- Site characteristics sites lacking suitable microorganisms to ferment the PED and/or sites that have certain geochemical conditions that inhibit biodegradation of target VOCs will require bioaugmentation and/or additional remedial measures.

3.0 PERFORMANCE OBJECTIVES

The performance objectives are summarized in Table 1. The Final Technical Report (Expeditionary Warfare Center [EXWC] and Geosyntec, 2014) provides detailed descriptions of each performance objective.

Table 1. Performance objectives.

Performance			
Objective	Data Requirements	Success Criteria	Results
Qualitative Perfo	ormance Objectives		
Ease of implementation (Section 3.1)	• Feedback from field crew on handling and operating requirements for PED technology and time required (particularly in comparison to traditional soluble non-PED donor injection).	PED amendment to the source area can be effectively achieved using readily available equipment.	Confirmed. PED was successfully introduced to the source area using readily available direct-push injection equipment, with a few extra precautions (e.g. bonding and grounding) for handling the pure nBA.
Ability to promote biodegradation (Section 3.2)	 Pre- and post-amendment VOC concentrations in groundwater. Microbial numbers. 	 Increases in the concentrations of dechlorination breakdown products. Increases in the numbers of dechlorinating bacteria. 	Confirmed. Sustained production of dechlorination products, even in presence of CFC113. Dehalococcoides ethenogenes (Dhc) numbers increased throughout both test plots.
Longevity of electron donor supply (duration of remediation) (Section 3.3)	 Time of operation compared to typical application of soluble non-PED donor. Concentrations of VOCs, nBA & n-butanol, lactate, volatile fatty acid (VFA), total organic carbon (TOC) and dissolved hydrocarbon gas (DHG) in groundwater. 	Supply of reducing equivalents is sustained for longer than a system using a non-partitioning donor, requiring less frequent donor amendment.	Confirmed. Donor present (as TOC & VFAs) throughout 8 months (up to one year) following PED injection, declining over course of operation. Sustained well beyond the point where initial injectate volume was extracted.
PED partitions into the DNAPL (Section 3.4)	Conservative tracer (bromide), nBA & n-butanol concentrations in groundwater following amendment.	 Reduced concentrations of nBA relative to the conservative tracer in extracted groundwater following amendment, indicating uptake by residual DNAPL. Change in concentration should be proportional to mass of residual DNAPL present. 	Confirmed. Cápiro, et al., 2011. Liquid- Liquid Mass Transfer of Partitioning Electron Donors in Chlorinated Solvent Source Zones. Environ. Sci. Technol. 15;45(4):1547-54
PED partitions out of the DNAPL at a suitable rate and concentration (Section 3.5)	 PED concentrations in groundwater following amendment. VFA & TOC concentrations in groundwater. 	Observe sustained concentrations of nBA (and products), sufficient concentrations of electron donor to promote dechlorination, and microbial dechlorination products in extracted groundwater.	Confirmed. Sustained concentrations of electron donor (TOC and VFAs) were observed, with production of dechlorination products. Microbial numbers also increased.

Table 1. Performance objectives (continued).

Performance	5.5		- ·
Objective	Data Requirements	Success Criteria	Results
	formance Objectives		
Ability to deliver PED into the source area (Section 3.6)	 Injection parameter data and observations from field implementation regarding ability to deliver amendments to target zone. nBA and tracer concentrations in groundwater and nBA in soil samples following PED amendment. 	 Able to deliver desired volume of PED-amended fluid to target zone in a reasonable time (subject to limitations due to geology). Delivery of at least 75% of the target volume (33,600 gallons) of injectate. Concentrations of PED and tracer are well distributed following amendment. 	Success. Target volume and concentration of PED-amended fluid (33,600 gallons) was successfully injected to the target zones. PED and tracer were reasonably well distributed following amendment.
Increased DNAPL dissolution (Section 3.7)	Pre- and post-amendment VOC concentrations in groundwater	 Increase in total VOC mass flux to extraction wells. Total VOC concentrations (as parent-compound equivalents) will show greater enhancement factor than typical donor application (+50% compared with soluble). 	Generally Confirmed. Lower zone experienced an increase in total VOC mass flux to the extraction well. Upper zone did not show an increase in total VOC mass flux to the extraction well. Lower zone enhancement factor was in the range for a typical donor application.

4.0 SITE DESCRIPTION

4.1 SITE LOCATION

Hot Spot 1 is located at LC34 on CCAFS on the east-central Atlantic coast of Florida in Brevard County (Figure 1). Hot Spot 1 is a small TCE source area separate from the VOC mass beneath the ESB. The site is located east of the former ESB as shown on Figure 2. Prior to development, LC34 consisted of relict sand dunes and interdunal swales typical of barrier island depositional environments.

A full description of the site history, operations, investigations, and analytical results is detailed in the Resource Conservation and Recovery Act (RCRA) Facility Investigation (RFI) Report (NASA, 1999), RFI Addendum Report (NASA, 2003), and the Corrective Measures Study (CMS) Report (NASA, 2007).

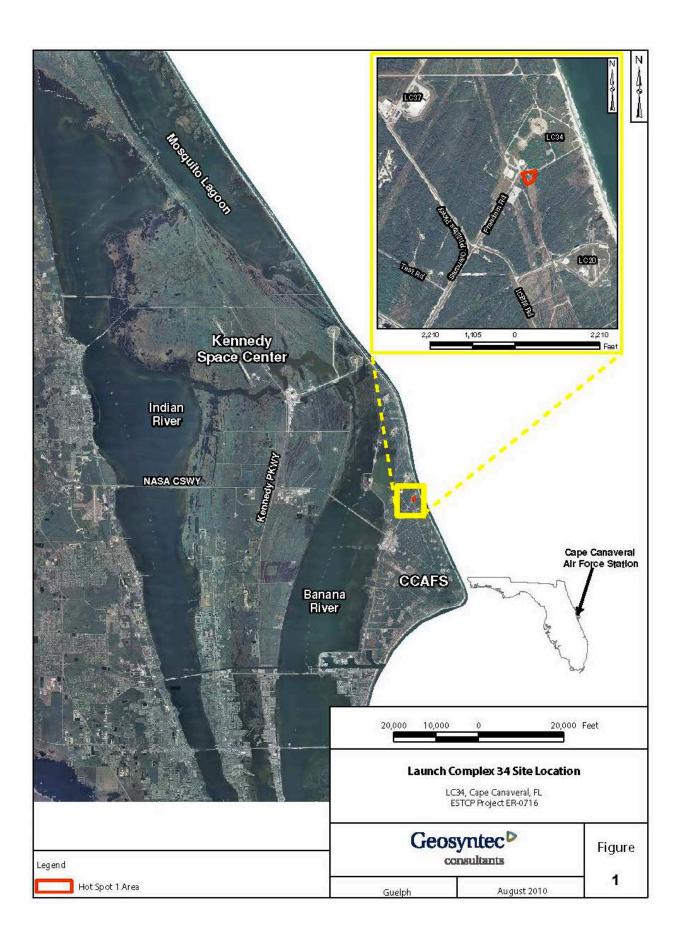
4.2 SITE GEOLOGY AND HYDROGEOLOGY

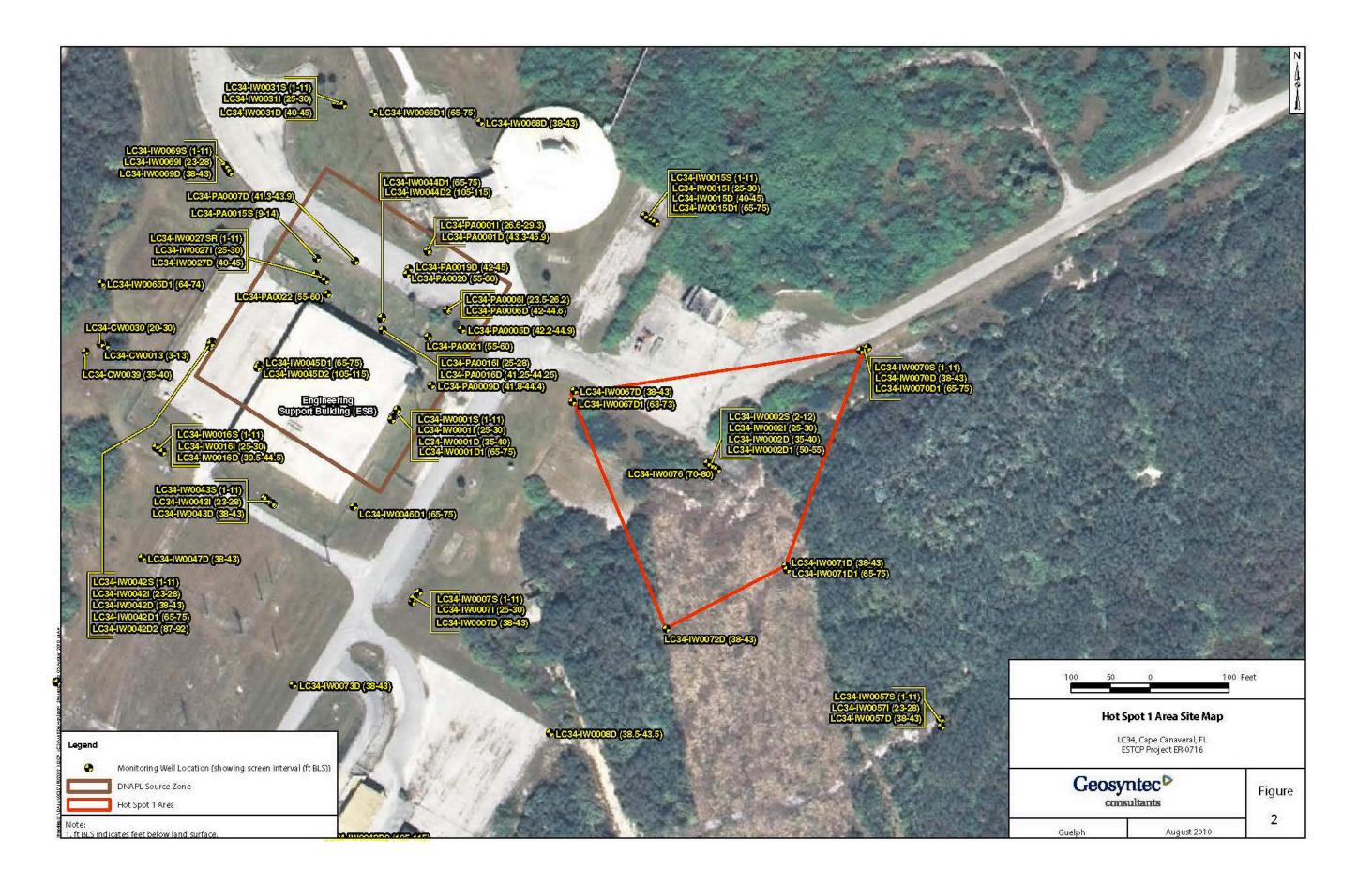
The site geology can be summarized as follows:

- Land surface to 45 feet below land surface (ft BLS): tan to gray, medium to very finegrained sands with varying amounts of shell fragments, with a hydraulic conductivity of 3 ft/day in the 30 to 45 ft BLS interval;
- 45 to 48 ft BLS (thickness varies): semi-confining unit comprised of silty sand to sandy clay with minor amounts of sand and shell fragments with a hydraulic conductivity of 10⁻³ to 10⁻⁴ ft/day;
- 48 to 60 ft BLS: medium light gray, medium to coarse-grained silty sand with abundant shell fragments with a hydraulic conductivity of approximately 2.8 ft/day (based upon pneumatic slug testing in 2009); and
- 60 to 80 ft BLS: homogeneous light olive gray, coarse to fine sands with a hydraulic conductivity of approximately 7.5 ft/day.

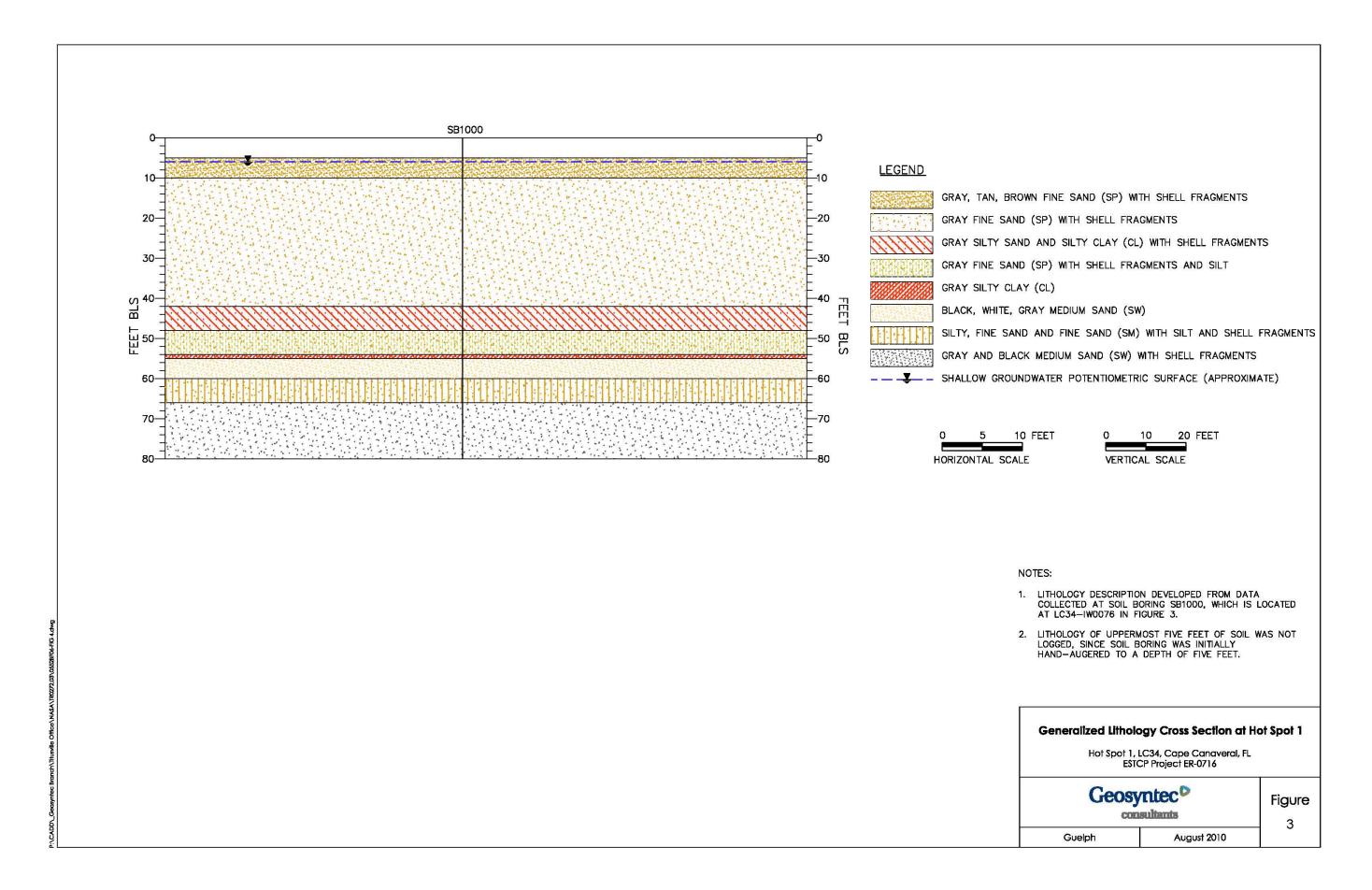
A continuous soil core was collected, using a sonic method, in the middle of the Hot Spot 1 area (SB1000, Figure 3). The core was consistent with general site lithology, with the exception of a second clay layer identified from 54 to 55 ft BLS. A full description of the general site lithology is detailed in the Final Technical Report (Geosyntec, 2013). A generalized litholgic cross section of the Hot Spot 1 area based on that core is shown on Figure 3.

Groundwater at the site is generally encountered at about 5 ft BLS. In the shallow island aquifer system found at LC34, surface water bodies influence groundwater flow. Two large water bodies, the Atlantic Ocean and the Banana River are located approximately 0.25 miles to the east and 1 mile west of the site, respectively. Period of record water levels indicate the primary direction of groundwater flow is directed to the coastal margins of the site with the highest recorded water levels near the area of the former ESB. At Hot Spot 1, which is south of the launch pad, groundwater flow in the shallow aquifer is predominantly to the east, toward the Atlantic Ocean. Groundwater gradients are relatively flat and in general, groundwater flow is











sluggish. Groundwater elevations show some tidal influence; apparent flow reversals may occur depending on tide stage at time of groundwater gauging. Groundwater potentiometric surface maps for the shallow aquifer from the 2008 and 2009 Annual Groundwater Monitoring Reports (NASA, 2009; NASA, 2010) are shown in Figure 4.

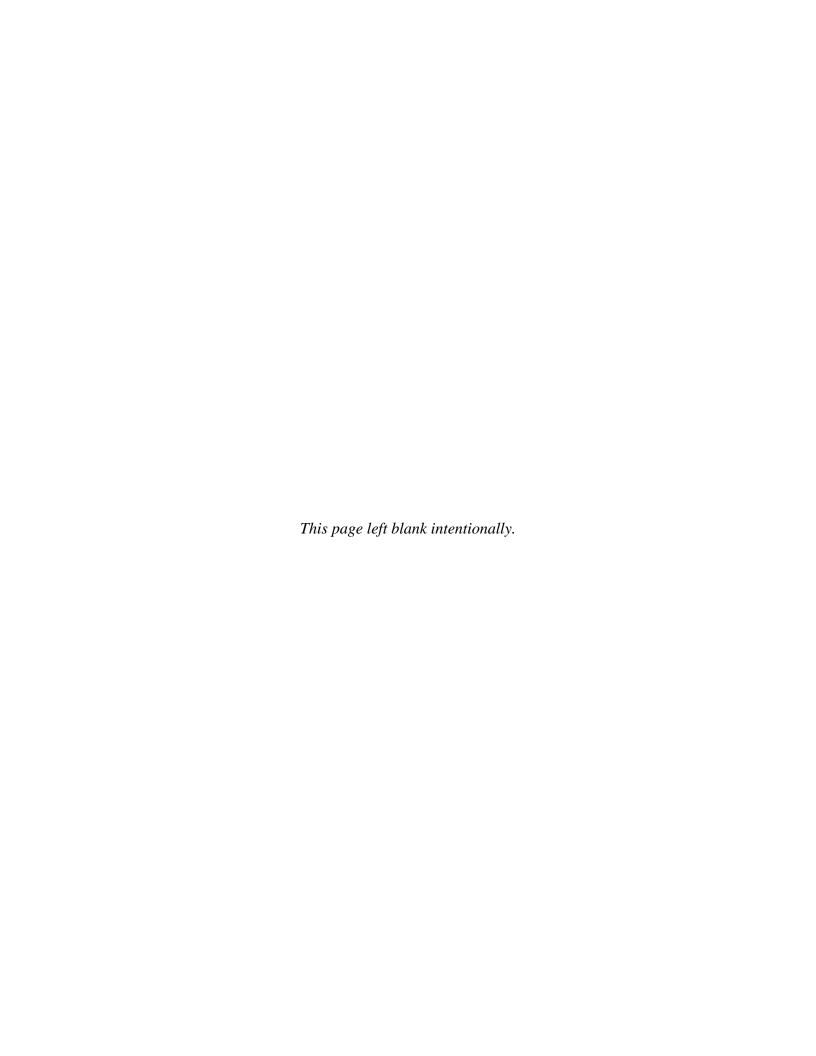
4.3 CONTAMINANT DISTRIBUTION

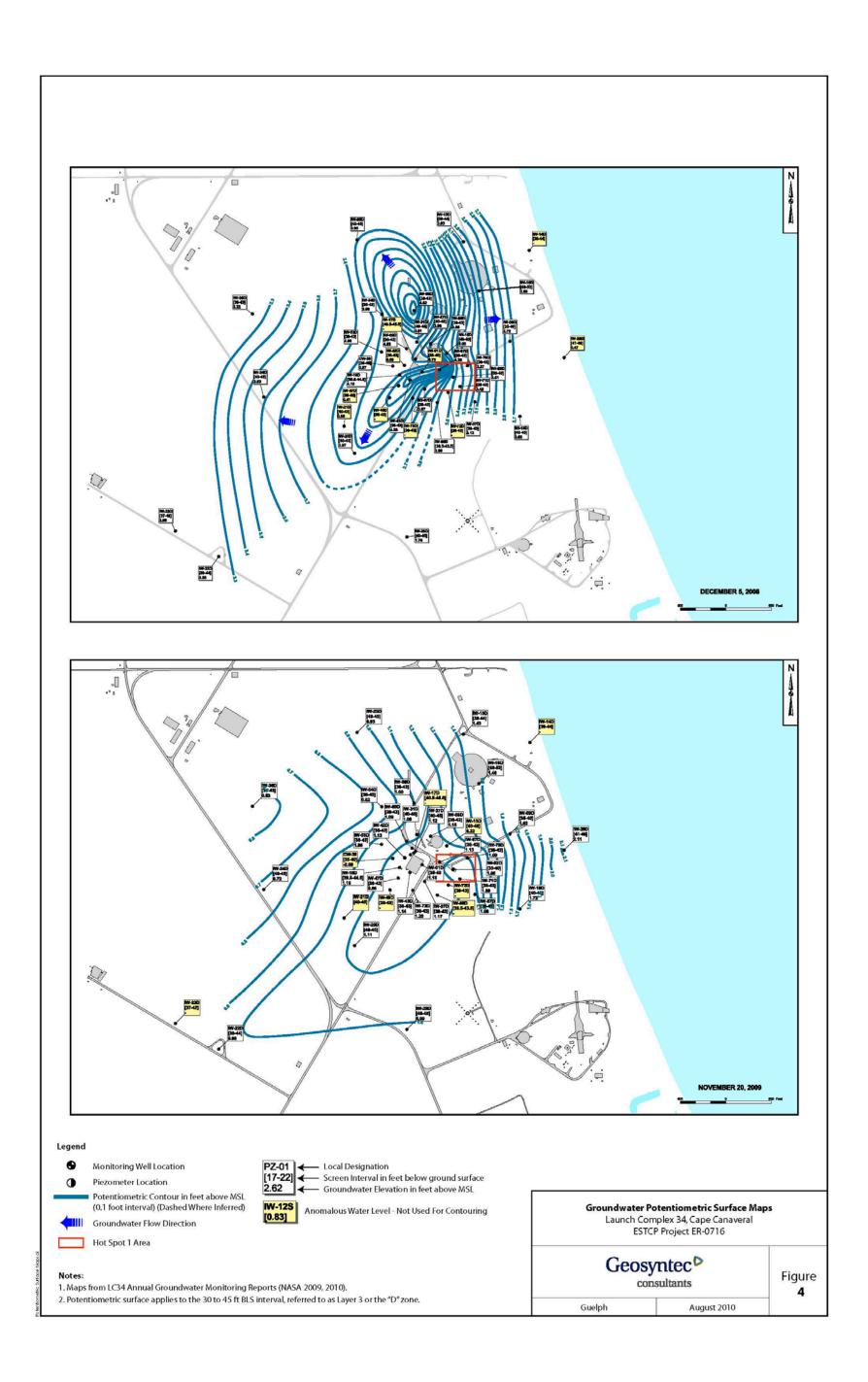
The Hot Spot 1 source mass is situated within the large VOC plume around the ESB. As a result, there are elevated levels of cDCE and VC that may not originate from the TCE in Hot Spot 1. The Hot Spot 1 TCE plume has been delineated to a concentration of 300 μ g/L; below this concentration the plumes are difficult to separate on the map due to comingling of the plumes. Although no other VOCs were identified in groundwater during prior routine monitoring of the existing monitoring wells, CFC113 was present at several locations in the upper aquifer at concentrations up to 130,000 μ g/L.

VOC impacts in the Hot Spot 1 area were delineated from 2008 to 2009 through a series of direct-push groundwater sampling events, a membrane interface probe (MIP) investigation, saturated zone soil sampling and installation and sampling of a deep monitoring well (screen interval of 70 to 80 ft BLS). MIP results were used in conjunction with the concentration data to define the vertical interval of VOC-impacted groundwater, which was deemed to be the 30 to 60 ft BLS interval for the PED DEM/VAL.

The CMS for the site (NASA, 2007) presents theoretical soil concentrations for TCE-DNAPL saturation. The maximum value measured, 56.2 milligrams per kilogram (mg/kg) dry, which is equivalent to 42.7 mg/kg in the bulk, is about 14% of the theoretical threshold value; hence, DNAPL is inferred to be present in the plot based on this result together with the groundwater concentrations.

The groundwater concentrations are indicative of a TCE-NAPL source: the source has been there for over 40 years and concentrations of TCE are still about $30,000~\mu\text{g/L}$ based on groundwater samples from the monitoring wells and direct push technology (DPT) samples in the middle of the Hot Spot 1 area.







5.0 TEST DESIGN

5.1 CONCEPTUAL EXPERIMENTAL DESIGN

The objective of the project was to DEM/VAL the application of a PED at a DNAPL source zone site to improve the biologically-enhanced dissolution rate of DNAPL over that which can be achieved with soluble, non partitioning electron donors. The overarching goal was to demonstrate that PED application offered increased bioremediation efficiency and decreased implementation costs. Figure 5 shows a cross section of the demonstration area. The Final Technical Report (Geosyntec, 2013) provides detailed information on the experimental design.

The PED technology was demonstrated at a source zone hot spot wherein TCE DNAPL is associated with a silty sand/silty clay horizon at about 42 to 48 ft BLS and TCE concentrations up to 141,000 µg/L had been reported (Figure 5). The hot spot was amended with PED nBA above, within and below this low permeability horizon. Two sweep zones, one above and one below the clay horizon were separately instrumented and operated, providing two data sets with which to evaluate the performance of the PED technology. Each sweep zone was instrumented with a single central extraction well, from which integrated groundwater samples were collected routinely to monitor the average concentration of various dissolved constituents over time. Extracted groundwater was returned to the aquifer through a set of ten groundwater injection wells on the perimeter of the TCE plume. At each of five injection locations, a pair of injection wells was installed, above and below the clay horizon, to help create an inward hydraulic gradient and promote horizontal flow across the top and base of the clay horizon.

Each extraction well operated at a relatively low flow rate to maintain an inward hydraulic gradient and collect representative groundwater from the aquifer on either side of the clay horizon. The extracted groundwater was analyzed for VOCs to establish the baseline flux of VOCs. Once baseline conditions were established, the zone was amended with electron donor nBA and conservative tracers (bromide and iodide) using DPT injection to deliver the amendments throughout the target zone. This approach delivered the amendment solution throughout the pore volume of the plot all at once, rather than relying on advective transport in a recirculation mode, and allowed the amendments to be preferentially delivered to the clay layer and the portions of the overlying and underlying aquifers where residual DNAPL may occur. A shut-in period, with no groundwater extraction, was then observed, to allow native microbes to acclimate to the nBA and allow biomass to become established within the demonstration area. Following this, soil and groundwater samples were collected to establish the distribution of electron donor and tracer within each demonstration area.

Following the biomass growth shut-in period, groundwater extraction was re-initiated, with routine sample collection to assess the concentrations and flux of various compounds. Comparison of concentrations (VOCs, PED, tracers) in groundwater initially and over time extracted from the central wells will assess the "disturbance effect" of direct injection and evaluate the quantity of PED that was taken up by NAPL, sorbed or diffused into secondary porosity of the formation (where the NAPL also likely resides). Trends in the concentrations of various dissolved constituents in extracted water over time were used to understand changes in the flux of VOCs (and amended compounds). Soil sampling was conducted before (baseline delineation) and after the demonstration area was amended, to establish mass distribution within

the plots, and again after operation was halted, to assess changes over the DEM/VAL operation and correlate these results with the observed trends in groundwater concentrations.

Both sweep zones were monitored throughout the course of the demonstration (March 2011 to February 2012), to evaluate system performance and evaluate whether laboratory assessment data are useful to predict PED performance under field conditions. The performance was assessed in terms of VOC mass flux enhancement and compared with previous studies using typical, non-partitioning, soluble electron donors such as lactate.

5.2 BASELINE CHARACTERIZATION

VOC impacts in the source zone (Hot Spot 1 Area) were delineated from 2008 to 2009 through a series of direct-push groundwater sampling events, a MIP investigation, saturated zone soil sampling and installation and sampling of a deep monitoring well (screen interval of 70 to 80 ft BLS). Figure 6 shows sampling locations and TCE concentration isopleths in Hot Spot 1 for the depth interval from 30 to 60 ft BLS. This figure presents dissolved-phase TCE concentrations from both direct-push groundwater grab samples and from permanent monitoring wells prior to the PED DEM/VAL.

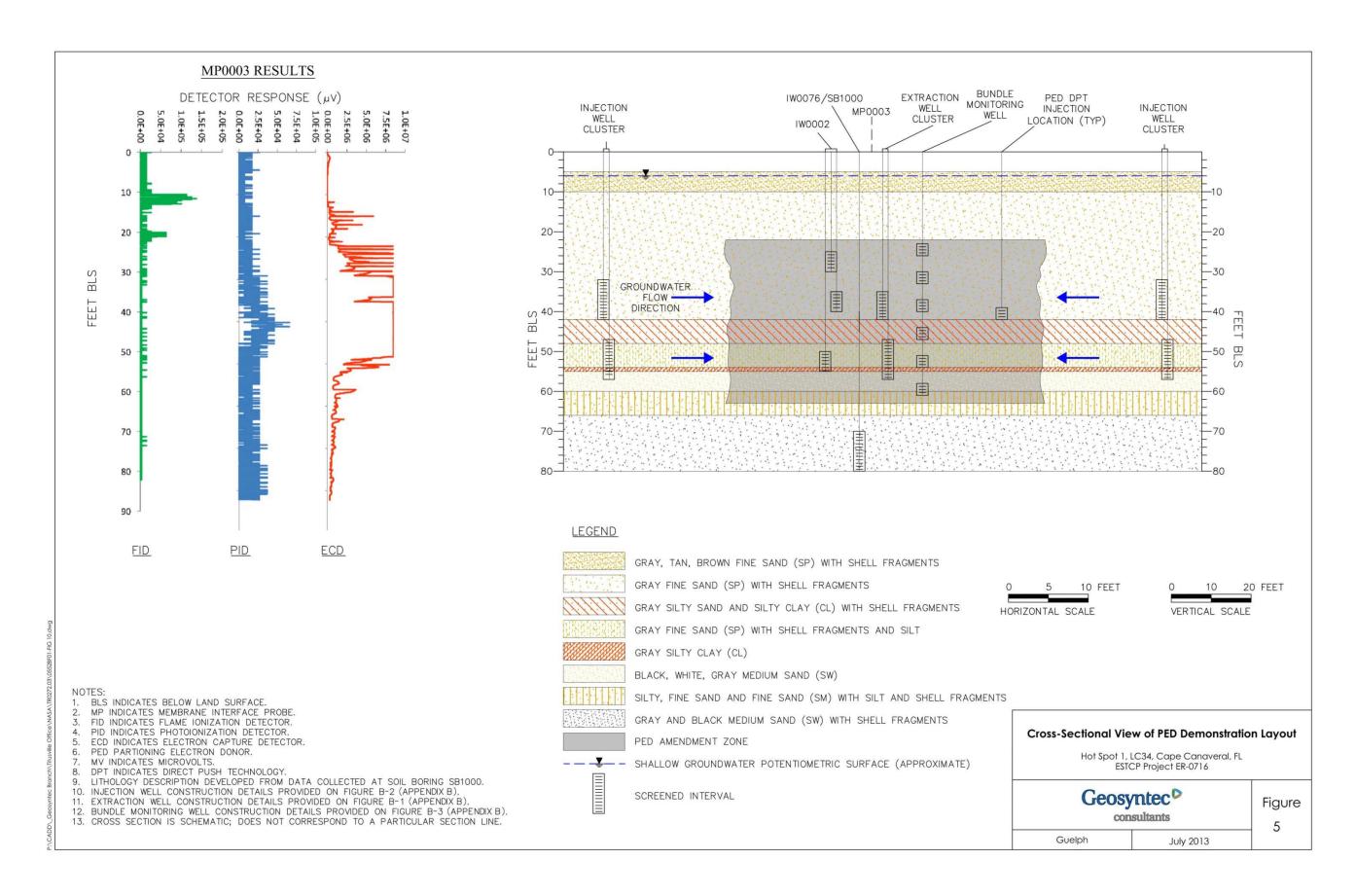
Soil samples were collected in the Hot Spot 1 area during sonic drilling to install a deep monitoring well (IW0076, screen interval from 70 to 80 ft BLS) proximal to IW0002D and MIP0003. Continuous core was collected and logged to a depth of 80 ft BLS. Six discrete saturated zone soil samples (5 grams [g] each) were collected to assess TCE concentrations above, in and below the clay confining layer. The results were presented in the Technology Demonstration Plan (TDP); Lebrón and Major, 2011). The TCE mass distribution was consistent with the MIP logs and groundwater data, as shown in Figure 6.

5.3 TREATABILITY OR LABORATORY STUDY RESULTS

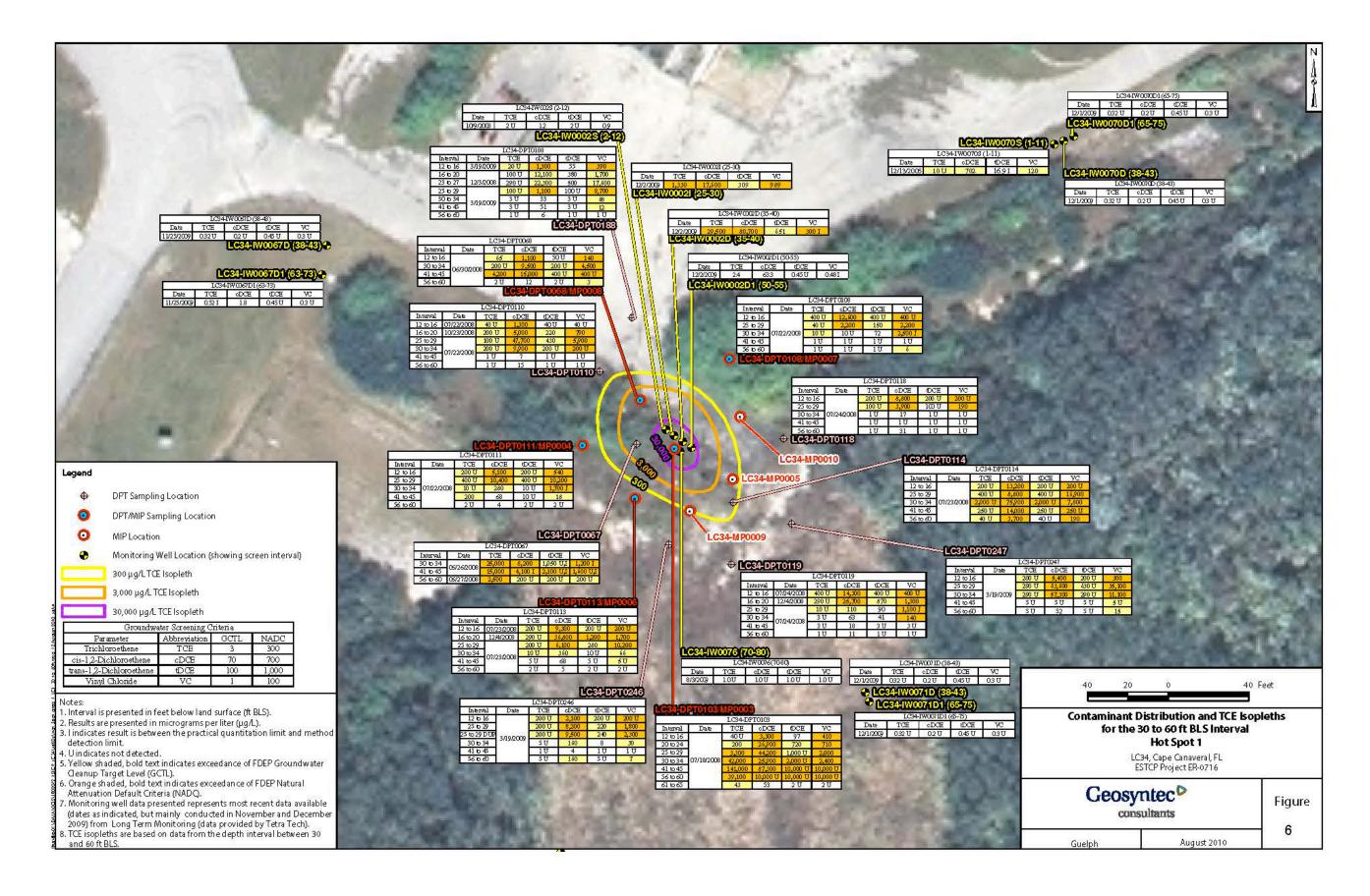
A Laboratory Treatability Report (NAVFAC ESC et al., 2010) was prepared for the Environmental Security Technology Certification Program (ESTCP) review committee to present the results of the Laboratory Treatability Testing conducted as part of ESTCP project ER-200716. Laboratory treatability studies were conducted to evaluate candidate PEDs for eventual field application as part of the project.

Liquid-liquid equilibrium batch tests indicated that the partitioning behavior of both candidate PEDs (nHEX and nBA) could be characterized by ideal linear partitioning theory over the range of aqueous concentrations likely to be used in a field application (i.e. using initial dissolved-phase concentrations approaching aqueous solubility of the PED). Results demonstrated that based on partitioning coefficients nBA would partition more strongly into the NAPL than the nHEX. nBA was selected for the field application (Capiro et al., 2011).

Microbial batch studies confirmed the efficacy of nBA as the electron donor to support the KB 1[®] Plus consortium to dechlorinate TCE and 1,1,1-trichloroethane (1,1,1-TCA). The results indicated that the KB 1[®] Plus consortium was able to degrade nBA and utilize it as an electron donor for dechlorination of TCE and 1,1,1-TCA.









5.4 FIELD TESTING

The field DEM/VAL was implemented in accordance with the Demonstration Plan. Implementation of the experimental design consisted of seven main tasks as follows:

- a. Installation and Shake Down (Task 1);
- b. Baseline Soil and Groundwater Sampling (Task 2);
- c. Baseline Flux Assessment (Task 3);
- d. Introduction of PED and Tracers (Task 4);
- e. Biomass Growth (Task 5);
- f. Recirculation System Operation (Task 6); and
- g. Demobilization (Task 7).

Table 2 presents a summary of the type and number of samples collected from each phase of the DEM/VAL. Figure 7 provides a Gantt chart of the technology demonstration schedule. Further detailed explanations of the field testing can be found in the Final Technical Report (Geosyntec, 2013).

5.5 SAMPLING METHODS

Table 2 summarizes the number and frequency of sample collection, types of samples, and analytes of interest. No specialized analytical sampling methods were used.

5.6 SAMPLING RESULTS AND ANALYSIS

Detailed sampling results are provided in the Final Technical Report (NAVFAC and Geosyntec, 2014) and include appendices with information on system installation and baseline characterization, operations summary, sampling program tables, data summary, quality assurance (QA)/quality control (QC), and laboratory and analytical reports. A brief summary of key results obtained from the PED evaluation is provided below.

To characterize the baseline conditions, soil and groundwater samples were collected within the treatment zone. Soil samples were collected during well installation activities. Groundwater sampling included: a) an initial synoptic event (Task 2) to determine the initial VOC distribution within the demonstration area following well construction; b) routine sampling of the extraction wells and selected monitoring locations during recirculation to establish the baseline flux of VOCs (Baseline Flux Assessment Phase, Task 3); and c) a synoptic event to determine the VOC distribution at the end of the Baseline Flux Assessment Phase (Task 3).

A summary of the key operational and system details are as follows:

• In baseline recirculation, in the upper zone, 58.6 kilogallons (kgal) were recirculated at an effective average flow rate (i.e., total volume divided by total time) of 1.16 gallons per minute (gpm), representing approximately 2.3 pore volume exchanges of the PED injection zone. In the lower zone, the cumulative volume of groundwater recirculated was 44.0 kgal, representing approximately 1.7 pore volume exchanges of the PED injection zone. The effective average flow rate for the system was 0.87 gpm.

- The PED injection was completed as planned. Fluid containing PED and tracers was amended throughout the demonstration area via 20 DPT injection locations. A total of 34,000 gallons (1,700 gallons per injection point) of fluid containing 3,000 milligrams per liter (mg/L) of nBA was injected into the target depth interval from 23 to 62 ft BLS. Injection rates typically ranged from 6 to 8 gpm, requiring pressures of 30 to 45 pounds per square inch (psi).
- Based on the target depth intervals, 50% of the total volume, or 17,000 gallons of injectate, was amended to the upper sweep zone; 15% of the volume (5,100 gallons) was amended within the silty clay horizon; and 35% of the volume (11,900 gallons) was amended to the lower sweep zone.
- A total of roughly 11.6 kilograms (kg) of potassium bromide (KBr) was introduced to the treatment area, resulting in 3.9 kg of bromide to the upper sweep zone, 1.2 kg within the silty clay horizon and 2.7 kg to the lower sweep zone. A total of about 11.7 kg of potassium iodide (KI) (8.9 kg of iodide) was added to the 17,000 gallons introduced into the upper zone.
- The Main Recirculation Phase occurred between 09 August 2011 and 16 February 2012. The recirculation systems generally operated as designed. In the upper zone, 243.4 kgal were recirculated at an effective average flow rate (i.e. total volume divided by total time) of 0.89 gpm. With flow divided between five injections wells, the average effective injection rates were approximately 0.17 gpm per injection location. Overall, the system was active for about 53% of the time.
- Following the Main Recirculation Phase, the recirculation system was operated for an additional seven months, from 17 February 2012 through 13 September 2012, under an Interim Measure Work Plan (IMWP) for NASA. System operation was essentially the same as during the prior phase. The recirculated volume for the upper sweep zone was 240.9 kgal, representing an additional sweep zone 1.9 pore volumes, or approximately 9.5 additional exchanges of the PED injected area. In the lower sweep zone, the recirculated volume was 239.2 kgal, representing an additional 1.8 pore volumes, or approximately 9.5 additional exchanges of the PED injected area.

A standard application injection of the PED would have left the PED in place and treatment would be under ambient (i.e., unpumped) conditions. It was solely for the purposes of the DEM/VAL, to evaluate longevity and quantify effectiveness, that extraction of groundwater was conducted. During this phase the majority of the PED occurred as n-Butanol (nBuOH), indicating that the nBA had undergone considerable hydrolysis during this stage. Data indicated consumption of the PED was due to microbial activity. The VOC concentrations in this phase indicate considerable reductive dechlorination activity. The biomass growth stage verified that PED injection with the direct push approach was able to provide additional donor and promote dechlorination. Figure 8a and 8b shows the operating history for extraction wells RW0007 and RW0008.

Table 2. Total number and types of samples collected. Hot Spot 1, LC34, CCAFS/ESTCP Project ER-2000716

		Number of					
Stage	Matrix	Samples	Analyte	Sampling Frequency/Location ⁽¹⁾			
		19	VOCs (includes nBA)	4 locations within test plot, 4 to 6 depths per location			
	Soil: Laboratory Measurement	8	Fraction of organic carbon	2 locations within test plot, 4 depths per location			
		4	Grain size distribution	4 samples from location SB1002			
	Groundwater: Field Measurement	NA	Field parameters (DO, ORP, pH, conductivity, temperature)	Data was recorded during all sample collection events			
	Water: Laboratory Measurement	6	VOCs (includes nBA and n-butanol)	Effluent samples from granular activated carbon treatment			
nent		94	VOCs (includes nBA and n-butanol)	Initial baseline from all wells including 6 perimeter wells and 4 injection wells; weekly from 2 RWs and 8 MWs for 3 weeks of recirculation; snapshot of all			
tage 2 – Baseline and – Baseline Flux Assessment		30	VFAs	Weekly from 2 RWs for 3 weeks during recirculation; snapshot of all locations except perimeter wells at end of one month of recirculation			
seline Flux A		30	Tracers (bromide and iodide)	Weekly from 2 RWs for 3 weeks during recirculation; snapshot of all locations except perimeter wells at end of one month of recirculation			
2 – Ba		36	TOC	Weekly from 2 RWs for 3 weeks during recirculation; snapshot of all locations except perimeter wells at end of one month of recirculation			
stage 2 – Bas	Groundwater: Laboratory Measurement	26	DHGs	Biweekly samples from 2 RWs during recirculation (i.e., after about 2 weeks), and snapshot of all locations except perimeter wells at end of one month of recirculation			
Stage 3 -		15	Hydrogen sulfide	Biweekly samples from 2 RWs during recirculation (i.e., after about 2 weeks), and snapshot of 2 RWs and 11 MWs at end of one month of recirculation			
<u>N</u>		15	Anions	Biweekly samples from 2 RWs during recirculation (i.e., after about 2 weeks), and snapshot of 2 RWs and 11 MWs at end of one month of recirculation			
		15	Alkalinity	Biweekly samples from 2 RWs during recirculation (i.e., after about 2 weeks), and snapshot of 2 RWs and 11 MWs at end of one month of recirculation			
		12	Dissolved metals	Sampling at the end of one month of recirculation from 2 RWs and 11 MWs			
		6	Microbial characterization (Dhc 16S rRNA gene/vcr A)	Sampling at the end of one month of recirculation from 2 RWs and 4 MWs			
	Groundwater: Field Measurement	NA	Field parameters (DO, ORP, pH, conductivity, temperature)	Data was recorded during all sample collection events			
age 4 PED Injection	Water	17	VOCs (includes nBA and n-butanol)	Samples from selected batches of PED injection fluid			
4 2		17	Tracers (bromide and iodide)	Samples from selected batches of PED injection fluid			
Stage Inje	Groundwater: Laboratory	29	VOCs (includes nBA and n-butanol)	Following PED injection, DP sample collection at 4 step-out locations, with 4 to 5 depths each; sampling at 11 select MWs			
St	Measurement	25	Tracers (bromide and iodide)	Following PED injection, DP sample collection at 4 step-out locations, with 4 to 5 depths each; sampling at 11 select MWs			
	Soil: Laboratory Measurement	17	VOCs (includes nBA and n-butanol)	3 locations from test plot, 5 to 6 depths per location			
Ę.	Groundwater: Field Measurement	NA	Field parameters (DO, ORP, pH, conductivity, temperature)	Data was recorded during all sample collection events			
Growth	Groundwater: Laboratory Measurement	24	VOCs (includes nBA and n-butanol)	Snapshot following shut-in period, all locations except perimeter wells			
Ğ		24	VFAs	Snapshot following shut-in period, all locations except perimeter wells			
		24	Tracers (bromide and iodide)	Snapshot following shut-in period, all locations except perimeter wells			
Biomass		24	TOC	Snapshot following shut-in period, all locations except perimeter wells			
		24	DHGs	Snapshot following shut-in period, all locations except perimeter wells			
\sim		13	Hydrogen sulfide	Snapshot following shut-in period, subset of locations (2 RWs, 11 MWs)			
Stage		13	Anions	Snapshot following shut-in period, subset of locations (2 RWs, 11 MWs)			
St		13	Alkalinity	Snapshot following shut-in period, subset of locations (2 RWs, 11 MWs)			
		12	Dissolved metals	Snapshot following shut-in period, subset of locations (2 RWs, 11 MWs)			

Table 2. Total number and types of samples collected (continued).

Hot Spot 1, LC34, CCAFS/ESTCP Project ER-2000716

		Number of		
Stage	Matrix	Samples	Analyte	Sampling Frequency/Location ⁽¹⁾
	Soil: Laboratory Measurement	22	VOCs (includes nBA and n-butanol)	3 locations within test plot, 7 to 8 depths per location
_	Groundwater: Field Measurement	NA	Field parameters (DO, ORP, pH, conductivity, temperature)	Data was recorded during all sample collection events
ystem		84	VOCs (includes nBA and n-butanol)	2 RWs weekly for one month, biweekly for five months; snapshot at month 3 of all locations; snapshot at month 6 of all locations
Sysı		72	VFAs	2 RWs weekly for one month, biweekly for five months; snapshot at month 3 and month 6 of all locations except perimeter wells
S uo		72	Tracers (bromide and iodide)	2 RWs weekly for one month, biweekly for five months; snapshot at month 3 and month 6 of all locations except perimeter wells
ulatio		78	TOC	2 RWs weekly for one month, biweekly for five months; snapshot at month 3 of all locations except perimeter wells; snapshot at month 6
circulation . Operation	Groundwater: Laboratory			of all locations
ecirc Ope	Measurement	72	DHGs	2 RWs weekly for one month, biweekly for five months; snapshot at month 3 and month 6 of all locations except perimeter wells
Re	Wicasurement	50	Hydrogen sulfide	2 RWs weekly for one month, biweekly for five months; snapshot at month 3 and month 6 from subset of locations (2 RWs, 11 MWs)
9 e		50	Anions	2 RWs weekly for one month, biweekly for five months; snapshot at month 3 and month 6 from subset of locations (2 RWs, 11 MWs)
Stage		50	Alkalinity	2 RWs weekly for one month, biweekly for five months; snapshot at month 3 and month 6 from subset of locations (2 RWs, 11 MWs)
N.		48	Dissolved Metals	2 RWs weekly for one month, biweekly for five months; snapshot at month 6 from subset of locations (2 RWs, 10 MWs)
		12	Microbial characterization (<i>Dhc</i> 16S rRNA gene/ <i>vcr</i> A)	Snapshot at month 3 and month 6, from 2 RWs and 4 MWs
	Soil: Laboratory Measurement	22	VOCs (includes nBA and n-butanol)	3 locations within test plot, 7 to 8 depths per location
7 Interim Measure irculation System Operation	Groundwater: Field Measurement	NA	Field parameters (DO, ORP, pH, conductivity, temperature)	Data was recorded during all sample collection events
eas	Groundwater: Laboratory Measurement	64	VOCs (includes nBA and n-butanol)	2 RWs monthly for five months; snapshot at month 10 of all locations; snapshot at month 13 of all locations except perimeter wells
Sy		48	TOC	Snapshot at month 10 and month 13 at all locations except perimeter wells
on atic		48	DHGs	Snapshot at month 10 and month 13 at all locations except perimeter wells
nter lati		12	Microbial characterization (<i>Dhc</i> 16S rRNA gene/ <i>vcr</i> A)	Snapshot at month 10 and month 13, from 2 RWs and 4 MWs
7 In				
ge				
Stage 7] Recirci				

Notes:

(1) There are 23 sampling locations (wells) within the treatment zone, including 2 RWs, 3 existing MWs, 3 nested multilevel MWs with 6 screen depth intervals each. There is 1 existing MW screened below the treatment zone. There are 3 far-field locations on the perimeter, each with a pair of wells screened above and below the clay horizon. Of the 10 injection wells, 4 were sampled at baseline. In addition, several DP locations were used for soil and groundwater sampling.

Dhc = DehalococcoidesnBA = n-butyl acetate

DHG = dissolved hydrocarbon gas ORP = oxidation reduction potential DO = dissolved oxygen PED = partitioning electron donor DP = direct push
GAC = granular activated carbon
MW = monitoring well RW = extraction well TOC = total organic carbon vcrA = vinyl chloride reductase enzyme

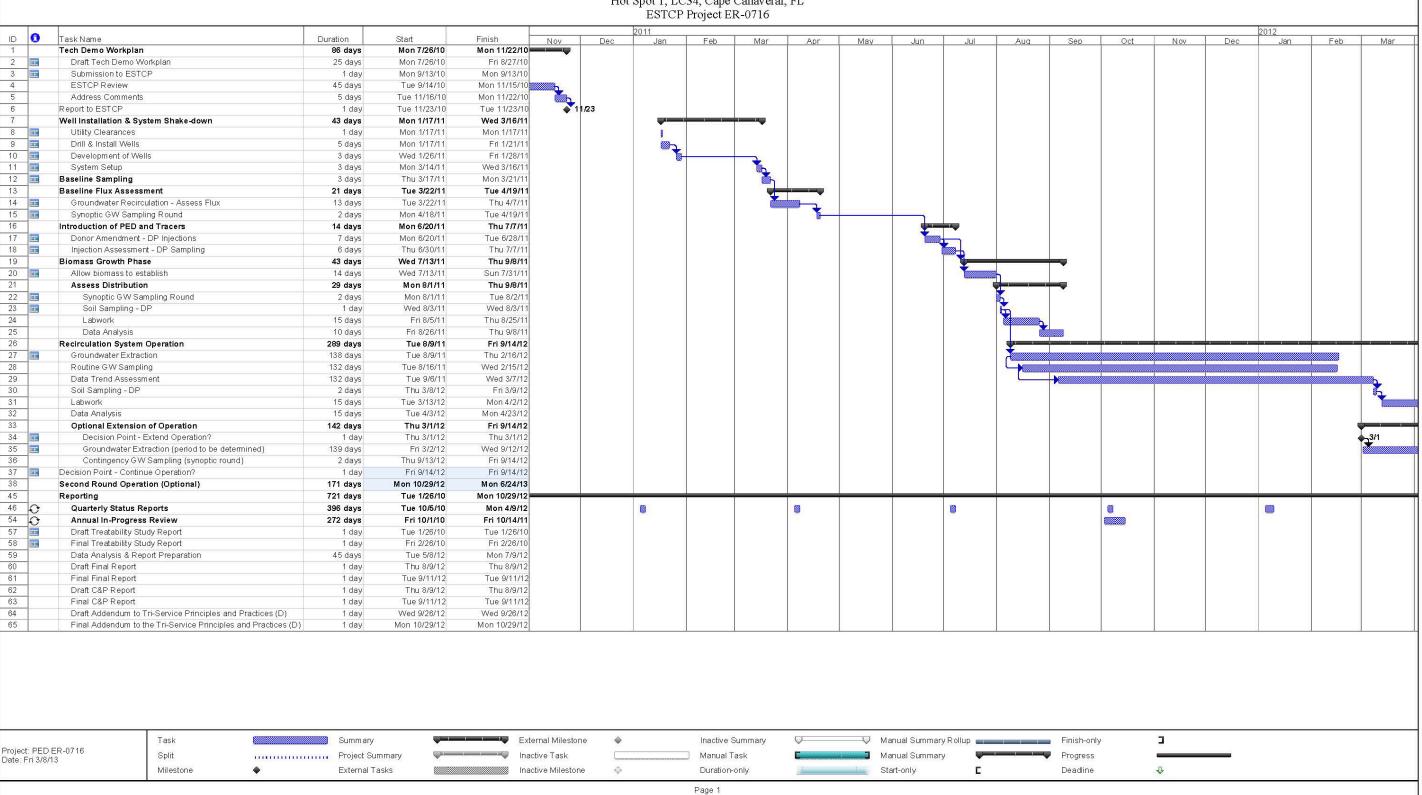
NA = not applicableVFA = volatile fatty acid

VOC = volatile organic compound

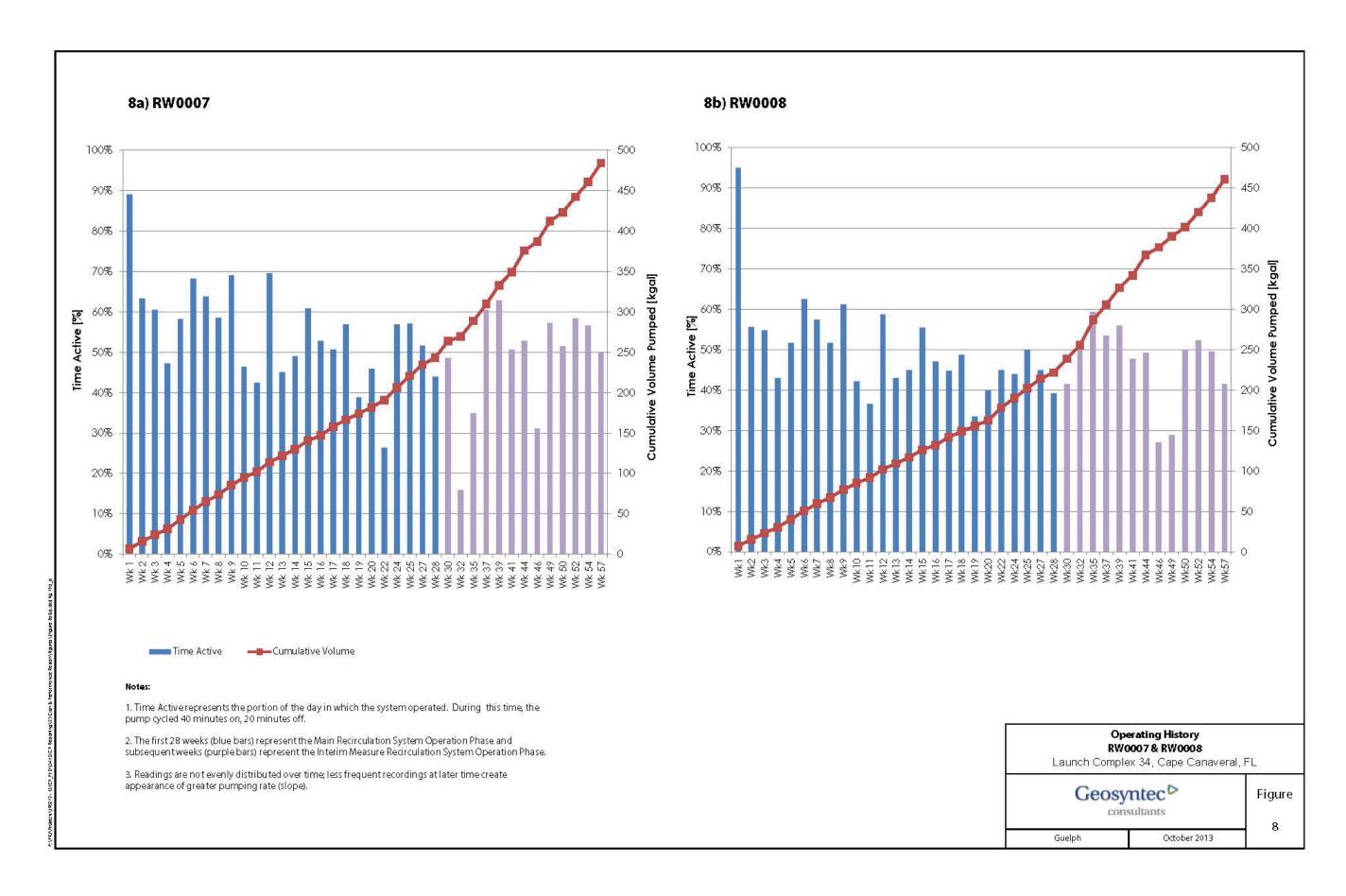
FIGURE 7 FIELD SCHEDUE

Geosyntec Consultants

Hot Spot 1, LC34, Cape Canaveral, FL









5.7 SOIL SAMPLING RESULTS

Figure 9 shows the interpolated TCE distribution before PED addition, incorporating prior data and the results of baseline sampling. Figure 10 shows the soil sampling locations for the baseline event and all subsequent soil sampling events. Figure 11 shows the location of the PED injection locations. Soils samples were collected at the end of the Main Recirculation Phase (Month 7) and at the end of the Interim Measure Recirculation Phase (Month 13). The sampling locations, shown in Figure 17, corresponded to the locations sampled following the Biomass Growth Phase, to facilitate comparison over the course of the DEM/VAL. Post PED injection, soil samples collected indicated PED was not present at the sampled locations. The PED, nBA, was only detected in a few locations, at very low concentrations. Minor amounts of nBuOH were observed in a couple of samples.

5.8 GROUNDWATER SAMPLING RESULTS

Groundwater samples collected from the central extraction wells (RW0007 and RW0008) make up the primary data set, which includes field parameters, VOCs, nBA, n-butanol, DHGs, VFAs, alkalinity, anions, dissolved metals, and microbial characterization numbers. Additional data was collected during synoptic events from the entire monitoring well network and used to support the interpretation.

For the upper zone, VOC data from the central extraction well RW0007 is presented as a time-series in Figure 12a, including the Initial Baseline and Baseline Flux Assessment results. Figure 12b presents the time-series VOC data for the lower zone from the central extraction well RW0008. Figure 13 shows the VOC distribution history for RW0007 and RW0008, respectively.

For the upper zone, Figure 13a illustrates that the total VOC flux to RW0007 during the Main Recirculation Phase was less than during the Baseline Flux Assessment Phase, whereas the PED was anticipated to increase the total volatile organic compound (TVOC) flux. During Baseline Flux Assessment weekly samples were collected to assess VOC concentrations under pumping conditions. The TVOC concentration and the VOC distribution were stable in the baseline flux phase, with cDCE being the primary VOC. The presence of cDCE is attributed to the larger VOC plume associated with the source area beneath the ESB (refer to Section 4 above). TCE and CFC113 concentrations were also stable (Figure 12a). The concentration of TCE had decreased considerably by the end of the Biomass Growth Phase as a result of PED addition. Over the course of the Main Recirculation Phase, TCE and cDCE concentrations decreased while VC and Ethene concentrations increased, indicating that reductive dechlorination was active. This trend continued through the Interim Measure Recirculation Phase. It is noted that the continued presence of CFC113 may have limited reaction rates in the upper zone.

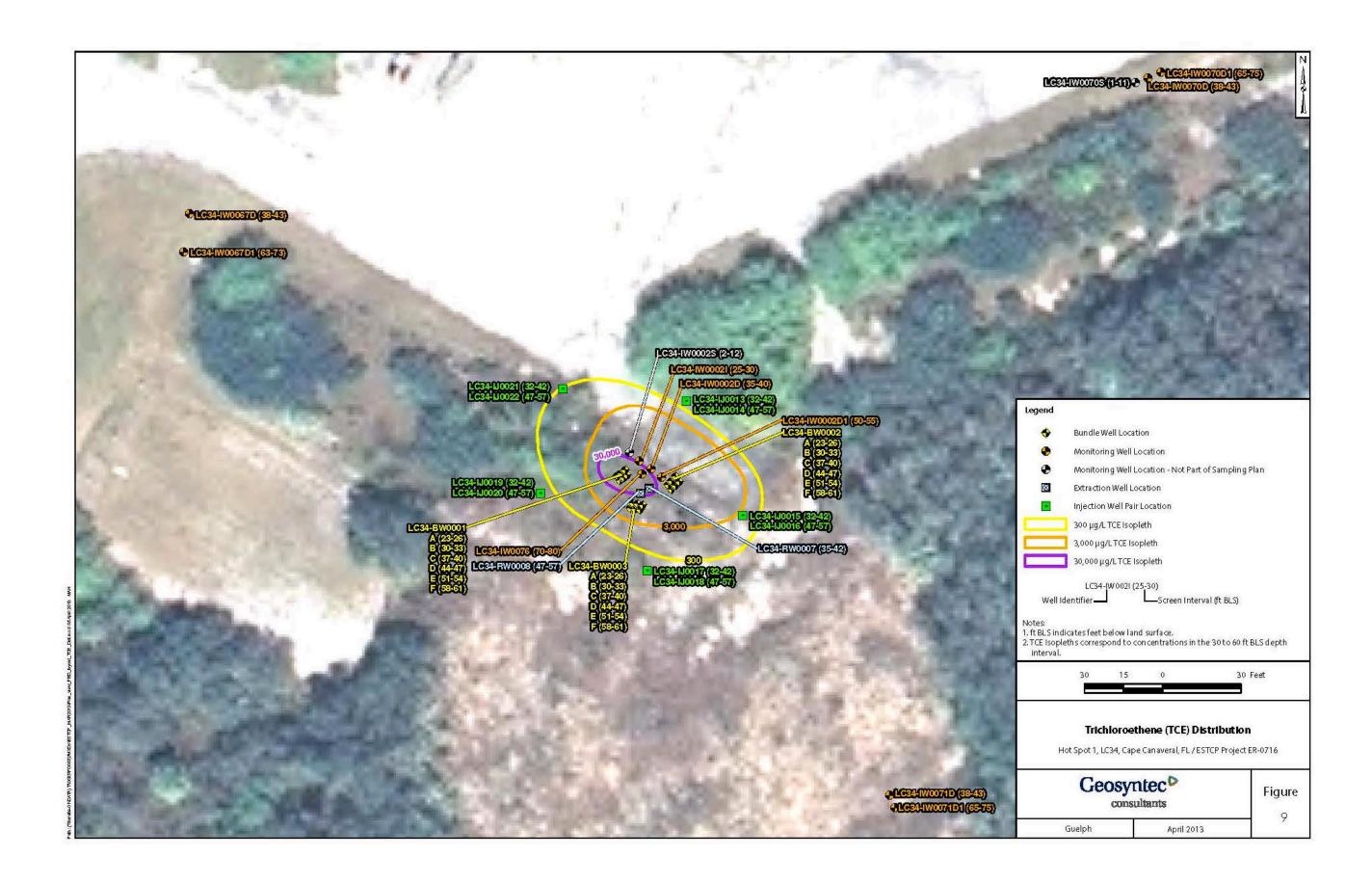
For the lower zone, Figure 13b illustrates that the total VOC flux to RW0008 during the Main Recirculation Phase was considerably greater than during the Baseline Flux Assessment Phase, indicating that PED addition increased the TVOC flux as anticipated. Note that the concentrations are considerably lower in the lower unit. During Baseline Flux Assessment weekly samples were collected to assess VOC concentrations under pumping conditions. The TVOC concentration and the VOC distribution were stable. TCE was the primary VOC and the cDCE concentration was about half that of TCE. The halo of the ESB plume was not observed in

the lower zone at Hot Spot 1. During the Biomass Growth Phase there were strong indications of reductive dechlorination activity. The confirmation samples in July 2011 indicated a significant increase in the TVOC concentration, primarily attributed to cDCE and then the samples at the end of the shut-in period indicated that all of the VOCs at RW0008 had been converted to VC and ethene. Once recirculation was started, groundwater containing TCE and cDCE was drawn to the well. Over the course of the Main Recirculation Phase, TCE concentrations fluctuated somewhat but did not sustain a concentration below baseline until the Interim Measure Recirculation Phase. Concentrations of less-chlorinated products, cDCE, VC and Ethene increased over the operation of the DEM/VAL, indicating that reductive dechlorination was active. This trend continued through the Interim Measure Recirculation Phase.

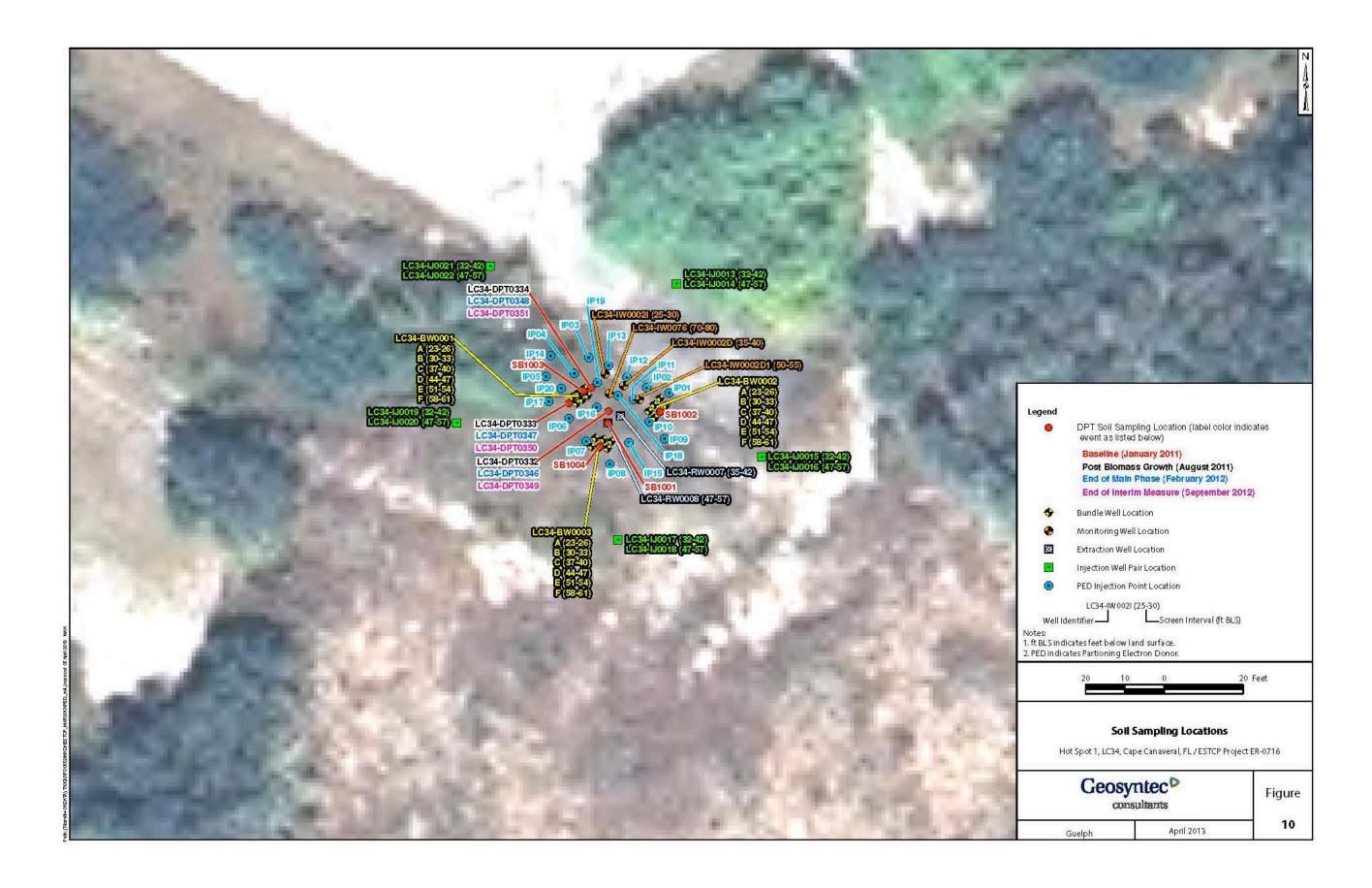
The extent of reductive dechlorination was characterized by calculating the fraction of chlorine removed from the equivalent concentration of TCE. The quantitative analysis of the extent of dechlorination is illustrated in Figure 14a for RW0007 and Figure 14b for RW0008, respectively. Note that complete conversion to DCE, VC, and ethene would correspond to dechlorination scores of 33%, 67% and 100%, respectively. These figures show that over the course of the DEM/VAL, both the upper and lower zones shifted increasingly toward complete dechlorination. The estimated TVOC mass in the treatment zone is based on the observed groundwater concentrations (Figure 15). The total mass of TCE, cDCE and VC is seen to decrease over the period of operation of the DEM/VAL.

5.9 EVALUATION OF DATA QUALITY INDICATORS

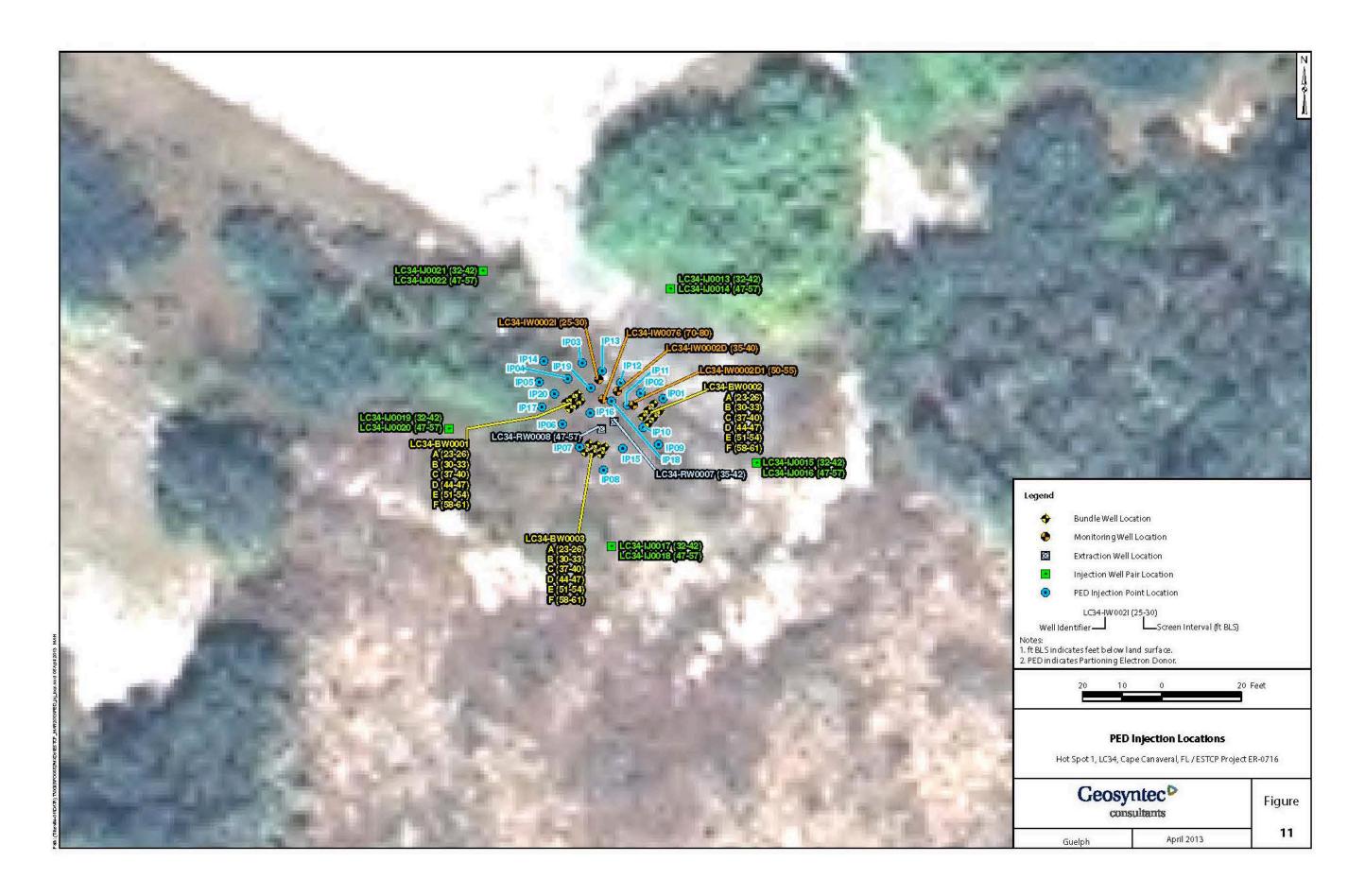
Data quality was assessed through evaluation of the data quality indicators (DQIs) precision, accuracy, representativeness, comparability, completeness, and sensitivity (PARCCS). Evaluation of the PARCCS data quality indicators was completed to ensure that data quality objectives were met. Field QA/QC data did not indicate any major data quality issues.



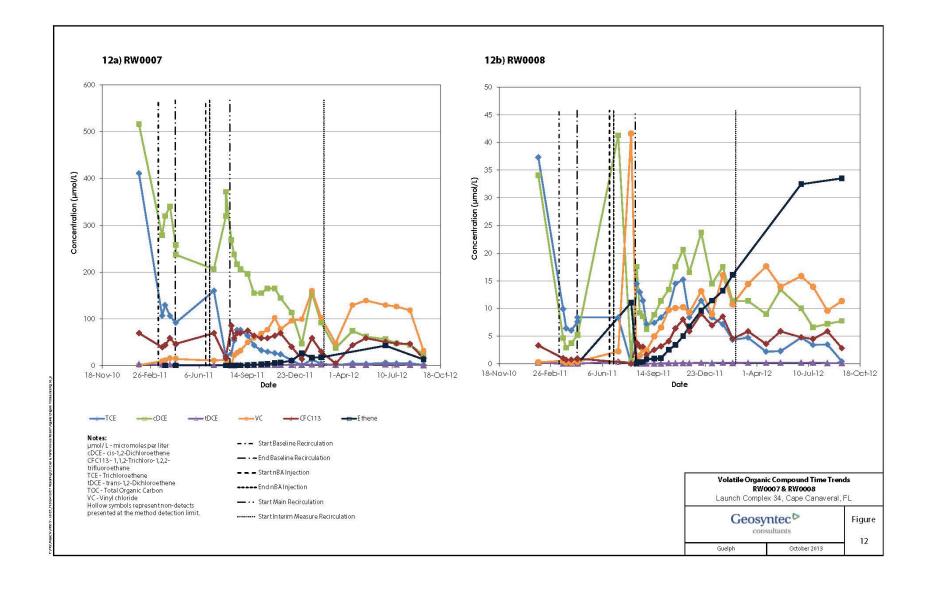


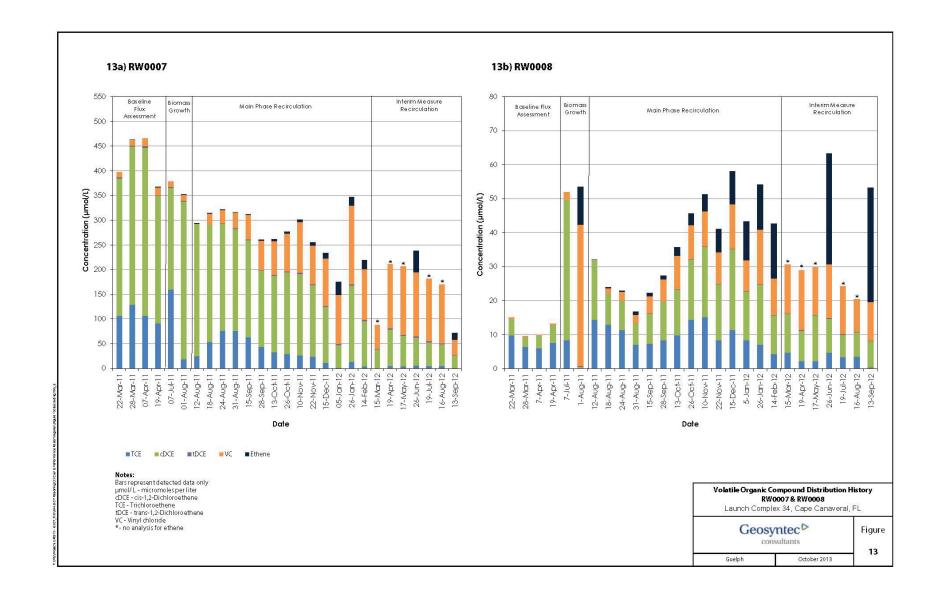


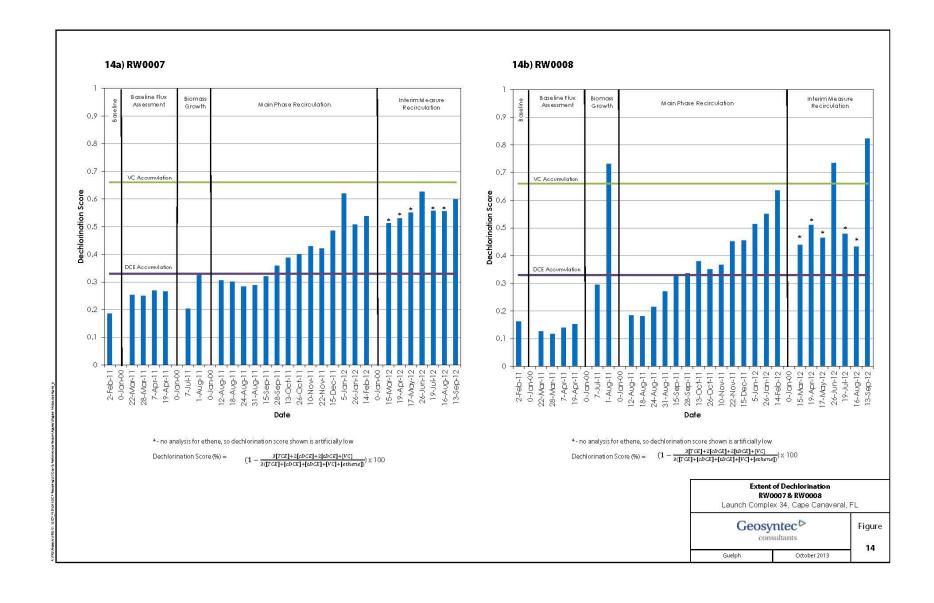


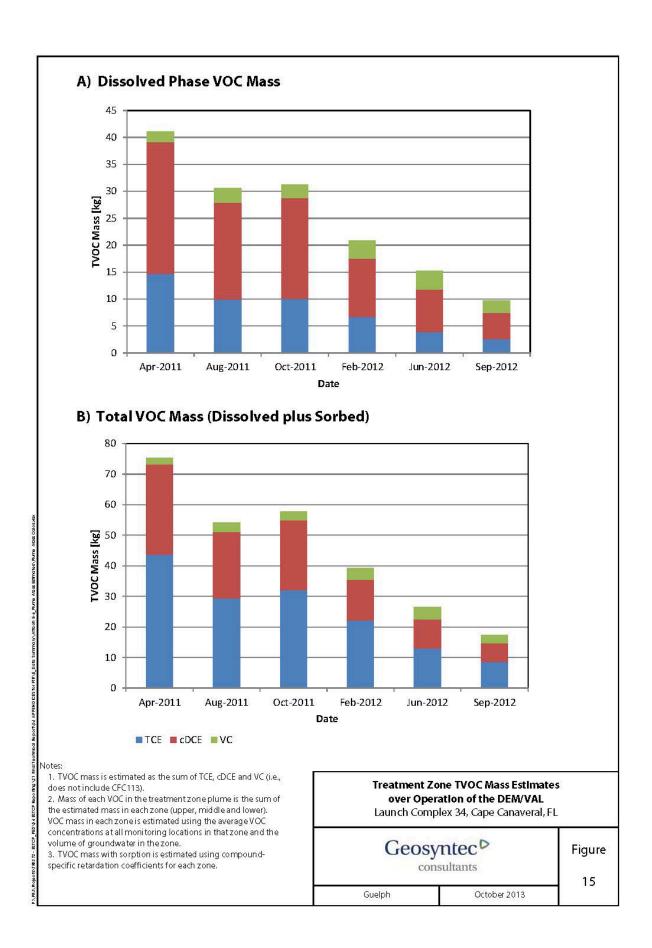












6.0 PERFORMANCE ASSESSMENT

Data analyses in support of the assessment of performance objectives is detailed in the Final Technical Report (NAVFAC EXWC and Geosyntec, 2014). A brief summary of Qualitative and Quantitative performance objectives are below.

6.1 EASE OF IMPLEMENTATION (QUALITATIVE)

To increase the likelihood that the PED technology will be adopted as an approach to source zone bioremediation, it should be straightforward to implement. The ease of implementation was evaluated based on the experience of field staff and the actual availability and costs of installed equipment. The success criterion for this objective is that PED amendment to the source area is effectively achieved using readily available equipment. This objective was achieved based on experience with the actual injection of nBA (the PED) at the Site. PED was successfully introduced to the source area using readily available direct-push injection equipment. Field application of nBA was deemed comparable to traditional soluble donor amendment in terms of equipment, time and effort, once the field crew were educated about nBA handling. The equipment required for the solar-powered recirculation system was also standard issue, readily available through local suppliers and assembled by technicians with training in basic plumbing techniques.

6.2 ABILITY TO PROMOTE BIODEGRADATION (QUALITATIVE)

To be effective, the PED must have promoted biodegradation of the target contaminants. The reduction in contaminant mass is a function of the degree to which biodegradation was promoted in the subsurface. The goal was to demonstrate that the PED (nBA) can be utilized by the native dechlorinating microorganisms and had the ability to promote biodegradation of TCE. The ability to promote biodegradation using the PED technology was evaluated on the basis of increases in the concentrations of dechlorination breakdown products and increases in the population of microorganisms capable of dechlorination (See figure 14). Groundwater samples were collected prior to donor amendment to establish baseline VOC concentrations and microbial numbers; groundwater samples were then collected over time during the demonstration to monitor changes in concentration and/or microbial numbers. In both the upper and lower demonstration areas, sustained production of dechlorination products, including ethene, was observed, demonstrating that the PED (nBA) could be utilized by the native dechlorinating microorganisms and thus had the ability to promote biodegradation of TCE.

6.3 LONGEVITY OF ELECTRON DONOR SUPPLY (QUALITATIVE)

Longevity of electron donor supply was assessed using the same time-series groundwater concentration data collected for assessment of several of the other objectives, namely the concentrations of remaining nBA, donor breakdown products (including n-BUT from nBA), VFAs, and TOC. Sustained donor supply from a one-time addition of PED is desirable, as it requires reduced frequency of donor replenishment. This objective was confirmed by the persistence of electron donor equivalents throughout the DEM/VAL operation (See Figure 15).

6.4 PED PARTITIONS INTO THE DNAPL (QUALITATIVE)

The partitioning of PED into DNAPL was evaluated using groundwater analyses for conservative tracers (bromide and iodide), nBA, nBuOH, and TOC following PED injection. This performance objective was met. Although data collected in the field DEM/VAL did not have sufficient resolution to demonstrate PED partitioning into DNAPL the partitioning phenomenon was clearly demonstrated in the laboratory column experiments (Cápiro et al., 2011 and the laboratory summary report). The major reason for the apparent difference in behavior, between laboratory and field, is the amount of NAPL present in each case.

6.5 PED PARTITIONS OUT OF THE DNAPL AT A SUITABLE RATE AND CONCENTRATION (QUALITATIVE)

The applied PED, once partitioned into residual DNAPL phases and onto sorption sites, must be released to groundwater at a rate and concentration that is sufficient to support bioremediation. The success of the technology relies on creating a sustained donor supply that matches the release of contaminants. The PED partitioning rate will be considered suitable if it occurs over the timeframe of the period of evaluation. This performance objective was considered met. Sustained concentrations of electron donor (TOC and VFAs) were observed, as well there was production of dechlorination products.

6.6 ABILITY TO DELIVER PED INTO THE SOURCE AREAS (QUANTITATIVE)

One objective of the PED DEM/VAL was to demonstrate that the PED can be readily delivered to the source area. In order to be an effective bioremediation approach, the application of PED should have been reasonably comparable to that of other traditional electron donors, so that its other properties can provide an overall benefit. The ability to deliver the design quantity of PED into the source area was expected to be comparable to that of other electron donors.

The objective was to be considered met if the design quantity of PED-amended fluid was delivered to the target zones within a reasonable amount of time (hours), using reasonable injection pressures. The success criterion was to emplace at least 75% of the target volume (33,600 gallons). This performance objective was met. The injection program successfully delivered the target volume and concentration of PED-amended fluid to the target zones: 34,000 gallons of injectate containing 3,000 mg/L nBA with bromide and/or iodide as tracers were injected.

6.7 INCREASED DNAPL DISSOLUTION (QUANTITATIVE)

The PED technology is designed to provide electron donor at the NAPL:water interface to promote growth of dechlorinating biomass as close to the source of dissolved-phase VOCs as possible. By promoting and supporting reductive dechlorination close to the NAPL:water interface, the PED creates a steep concentration gradient between the NAPL and the aqueous phases, which results in increased DNAPL dissolution.

The amount of DNAPL dissolution was assessed by comparing the mass discharge of VOCs before and after application of the donor. The mass discharge was calculated from the

groundwater VOC concentration data and the pumping rate and volume data. The total amount of TCE equivalents was calculated as the sum of TCE and its breakdown products, on a molar basis. It was expected that the PED plot would have increases in total VOC concentrations following amendment with nBA (relative to baseline). This increase in total VOC mass flux would be a primary indicator that the PED application worked as intended. The objective was to be considered met if the increase in total VOC mass flux observed in the PED plot was 50% or greater than that typically observed at sites where soluble donor was applied.

The result was partially confirmed. In the lower zone there was an increase in the total VOC mass flux to the extraction well (See Figure 12b). In the upper zone there was not an increase in total VOC mass flux to the extraction well (see Figure 12a). The lower zone enhancement factor was in the range for a typical donor application. DNAPL was not confirmed (i.e., observed) in the pilot test but the data collected indicate that there were additional TVOCs in the system.

6.8 IMPROVED EFFICIENCY OF ELECTRON DONOR UTILIZATION (OUANTITATIVE)

The efficiency of electron donor utilization was assessed using the groundwater concentrations of VOCs, electron donors, breakdown products, and DHGs over time. The parent donor compound, nBA, along with its breakdown products (n butanol, acetate, and other VFAs), were monitored, in addition to the VOCs and their breakdown products, plus other compounds that may have formed, such as methane, so that a detailed understanding of the donor consumption pathways was ascertained.

The objective would be considered met if the 'utilization ratio' is greater for PED than is typically observed with traditional soluble donors. The success criterion will be an observed increase in utilization ratio of 50% or greater relative to the soluble donor system of the prior LC34 study (Battelle, 2004; Hood et al., 2008).

The PED lasted longer than a soluble donor, several pore volume flushes were completed and if the donor was soluble it would have been extracted from the system. However, determining that the PED was more than 50% better than a soluble donor was not quantitatively determined. In the upper sweep zone significant cDCE was present at the start of the DEM/VAL and so production of cDCE from PED addition was not simply calculating the cDCE increase. This was not the case for the LC34 study. There were also elevated concentrations of CFC113 in many of the collected groundwater samples which can inhibit dechlorination which would also limit confirmation of the objective.

6.9 REDUCTION IN DNAPL MASS IN THE SOURCE AREA (QUANTITATIVE)

One goal of source zone bioremediation is to reduce the amount of DNAPL remaining in the source area, to reduce the expected time for clean-up. Reduced source mass may also result in reduced VOC loading to the downgradient plume. Assessment of this objective was based on the baseline and final VOC concentrations in soil and groundwater. If the PED is able to partition effectively into residual DNAPL and this promotes bioactivity then a decrease in soil VOC concentrations should occur. The objective was confirmed based on the interpolated TVOC mass in the treatment zone.

6.10 REDUCE OPERATION AND MAINTENANCE COSTS (QUANTITATIVE)

A major feature of the PED technology is the reduced frequency of donor replenishment, the commensurate reduction in application costs, and the shorter remedial timeframes, resulting in lower operation and maintenance (O&M) costs, anticipated due to increased rates of DNAPL dissolution. The success of the PED technology depends on the degree to which these reductions in the number of applications and in the cost of operation and maintenance can be realized.

The reduction in O&M costs was estimated on the basis of the data collected during the DEM/VAL, including the costs for materials, labor and analytical costs. The time of operation relative to operation with a soluble donor was extrapolated using apparent DNAPL dissolution rates to estimate remedial timeframe. The observed longevity was used to estimate the frequency of re-amendment, to estimate costs over the lifetime of the remedy.

This performance objective was generally confirmed. The PED remained longer in the groundwater compared to a simple soluble donor (e.g., lactate) and promoted dechlorination. After 8 months of recirculation there was still enough residual organic carbon to promote bioactivitiy. On this basis we can conclude that the donor lasted longer than estimated, with no significant biofouling issues and hence less frequent donor addition and maintenance with the PED over a soluble donor.

7.0 COST ASSESSMENT

To assess and validate the expected costs of the PED technology, detailed cost information was tracked during the demonstration. This provides a cost summary for implementation of the technology and for comparing it to potential alternative technologies. An effort was made to identify and track cost elements unique to the PED technology so that the cost benefits of the PED technology could be assessed and realistic cost estimates could be made for implementation at a given site.

7.1 COST MODEL

The simplified cost model developed for the PED technology is presented in Table 3. The cost model reflects the elements that were incurred in the demonstration and that would be required to implement the technology for site remediation. In most cases, costs for the demonstration were greater than those anticipated for a typical application, due to extra efforts to collect sufficient data during the demonstration to validate the technology. Costs for implementing the technology at a selected site can be estimated using standard costs for the elements.

Table 3. Cost model for application of partitioning electron donors. Hot Spot 1, LC34, CCAFS/ESTCP Project ER-200716

Cost Element	Data Tracked During the Demonstration	Estimated Costs	
Laboratory Treatability	Costs for collection of site soil and groundwater		\$100,000
Study	Costs for treatability study in lab	-	
	Materials	-	
	Labor costs		
	Laboratory analytical costs		
Infrastructure	Drilling (subcontractor)	Labor	\$33,534
Installation	Equipment costs	Expenses (including subcontractors)	\$57,080
	Labor costs		
Baseline	Laboratory analytical costs	Labor	\$4742
Sampling	DPT sampling (subcontractor)	Laboratory analytical	\$5175
	Labor costs	Expenses (including subcontractors)	\$806
Installation and	DP injection costs (subcontractor)	Labor	\$21,095
Amendment	Material costs – electron donor & tracer	Electron Donor	\$3065
	Labor cost	Tracers	\$2007
		Laboratory analytical	\$6484
		Expenses (including subcontractors)	\$59,810
Waste Disposal	Investigation derived waste disposal costs	Expenses	NA
O&M	Cost of labor for standard O&M	Labor	NA
	Additional materials or labor costs for troubleshooting, etc.	Expenses	NA
Performance	Labor costs	Labor	\$50,713
Sampling	DP soil sampling costs (subcontractor)	Laboratory analytical	\$69,606
	Laboratory analytical costs	Other expenses	\$15,261
Regulatory/ Permitting	Underground injection control (UIC) permit was obtained for NASA IMWP		
Total	2 2 2 2 2		\$429,377

7.1.1 Cost Element: Laboratory Treatability Study

Although not an absolute requirement, a treatability bench scale evaluation would be conducted at most sites to determine the feasibility of implementing bioremediation at the site and to determine whether bioaugmentation was required. The cost listed in Table 5 represents the large-scope treatability testing conducted at Georgia Tech as a component of this DEM/VAL. This level of testing would not be necessary to assess a candidate site for implementation of the PED technology. Instead, a relatively straightforward evaluation of the applicability of bioremediation at a given site would be performed, costs for which should be included to properly compare the PED bioremediation technology to other source zone remediation technologies. Typical treatability study costs include the costs for collecting site soil and groundwater, setting up microcosms, and sampling and laboratory analysis.

7.1.2 Cost Element: Infrastructure Installation

The costs for infrastructure installation included the construction of the monitoring, injection and extraction wells plus the solar-powered groundwater recirculation system. These costs will be somewhat site-specific, as the numbers of wells and the costs to install them will depend on site characteristics (e.g., depth of wells, lithology, size of source area, etc.). A recirculation system, solar-powered or conventional, is not required, but proved useful for the DEM/VAL. In practice, the PED technology could be implemented in a range of scenarios from passive (i.e., no recirculation) to fully active (continuous recirculation, with or without routine PED addition).

7.1.3 Cost Element: Baseline Sampling

Baseline sampling costs included costs for collection and analysis of soil and groundwater samples. In practice these costs will be somewhat site specific since the number of samples and target analytes will vary. It should also be noted, that costs for baseline sampling would apply regardless of technology selected for a site's remedial approach.

7.1.4 Cost Element: Installation and Amendment

This element included costs for the materials (nBA and tracers), PED injection (injection contractor, oversight) and confirmation sampling (sample collection, analytical). These costs can be expected to vary between sites.

DPT injection was used to deliver the PED into the subsurface throughout each pilot test area. This method of amendment delivery involved the costs for an experienced injection subcontractor (Vironex) and for oversight labor during installation. This included costs for suitable equipment and safety gear to properly handle the nBA in its pure form (e.g., bonding, grounding). Other than that, there were no costs that were unique to the PED technology.

The overall cost for implementation of the PED technology will depend on the required number of re-applications. This is reflected in the cost analysis below.

7.1.5 Cost Element: Waste Disposal

This is a standard cost element; hence, it was not tracked during the DEM/VAL. Typical investigation derived waste (IDW) disposal considerations will apply. In this case, NASA paid for disposal and the analytical costs for characterization were included with groundwater sample events.

7.1.6 Cost Element: Operation and Maintenance

No unique requirements were encountered. The costs for routine O&M during the DEM/VAL were not tracked separately, but are included in the Performance Sampling element (i.e., are included in Task 3 and Task 6 costs). Standard O&M costs can be used to estimate this element for full scale application of the technology.

7.1.7 Cost Element: Performance Sampling

Standard groundwater sampling and direct-push soil sample collection were used for monitoring the performance of the PED technology. The performance sampling costs were part of the demonstration assessment and were not typical for normal implementation of the PED technology. The costs for the detailed program were tracked and reported in Table 5, including labor, materials and laboratory analysis.

Some level of performance monitoring is required for any remedial technology. Since there are no unique sample collection or analytical requirements, the costs for a typical program can be estimated from standard monitoring costs for full scale application of the technology.

7.1.8 Cost Element: Regulatory/Permitting

The regulatory and permitting requirements are likely to vary from site to site, depending on the region and agency responsible for regulatory oversight. For the DEM/VAL, an UIC permit was obtained by NASA for their IMWP. The PED, nBA, may have an MCL in groundwater as it does in Florida. Estimates of typical costs for preparation of permit requests and permit fees can be used to estimate the cost of this element for full scale application of the technology.

7.2 COST DRIVERS

The costs to implement the PED technology for DNAPL source zone treatment will vary from site to site, depending on the size of the site (i.e., impacted volume) and several site-specific characteristics. The key cost drivers are listed below along with a brief discussion of the impact on cost.

- Area to be treated additional electron donor and DP locations would be required
- Depth of source area
- Vertical thickness
- Naturally occurring groundwater quality high concentrations of other electron receptors will increase the amount of donor required

DNAPL Mass and Distribution

Also consider:

- Lithology & permeability delivery in sands will be easier than in low permeability. Permeable (higher hydraulic conductivity) sites are likely to be better candidates for recirculation as a means of delivery and hydraulic control.
- Ambient groundwater velocity site with higher velocity will have greater flushing of donor and potential influx of additional electron acceptors, both of which may affect PED utilization

7.3 COST ANALYSIS

A comparison is made between the PED technology and the most comparable in situ source zone treatment technology, conventional source zone bioremediation using non-partitioning electron donors. A cost analysis was conducted to calculate expected costs to treat a hypothetical site with PED compared to using emulsified vegetable oil (EVO), a widely accepted electron donor. The hypothetical site was assumed to have the following characteristics:

- Sand aquifer (30% porosity) that is 30 feet (ft) deep and underlain by a clay aquitard;
- DNAPL source zone is 40 ft wide by 80 ft long by 15 ft deep (15 to 30 ft below ground surface [bgs]); and
- 500 kilograms (kg) of TCE DNAPL is present

Because PED is intended to be a source zone remedy, the cost comparison developed considers only treatment of the source zone and not the plume. For consistency, it is assumed that in both scenarios amendment of electron donor would occur via DP injection at 40 injection points, each with a 5 ft radius of influence, evenly distributed across the source area. For both scenarios, the target injection volume is 50% of the source zone volume, which is considered a realistic value to sufficiently distribute the applied donor (PED or EVO). The assumptions for the cost analysis are summarized in Table 4. The mass of donor required, frequency of injection and total treatment time were varied in accordance with the known properties of each donor. Complete source zone treatment requires a substantial amount of time. The analysis compares the PED and EVO approaches for initial source zone treatment, after which the two scenarios converge since beyond the initial timeframe further remediation may still be required, but each scenario would likely need similar efforts to complete treatment.

Table 4. Assumptions made for the basis of the cost analysis.

Hot Spot 1, LC34, CCAFS/ESTCP Project ER-200716

	PED		EVO	
	Value	Rationale	Value	Rationale
Assumed TCE mass (kg)	500	Assuming 0.1% NAPL would give a TCE mass of 310 kg. Using the soil concentration of 300 mg/kg (which if NASA's concentration indicative of NAPL) gives a TCE mass of 650. Based on these a mass of 500 kg was selected/assumed.	500	Assuming 0.1% NAPL would give a TCE mass of 310 kg. Using the soil concentration of 300 mg/kg (which if NASA's concentration indicative of NAPL) gives a TCE mass of 650. Based on these a mass of 500 kg was selected/assumed.
Stoichiometric donor demand	83	Based only on TCE mass.	63	Based only on TCE mass
Source zone volume (ft ³)	48,000	Assumes source zone is 40 ft wide, 80 ft long, and 15 ft thick	48,000	Assumes source zone is 40 ft wide, 80 ft long, and 15 ft thick
Depth of aquifer (ft bgs)	30	Assumption	30	Assumption
Source zone pore volume (ft ³)	14,400	Assumes porosity is 30%.	14,400	Assumes porosity is 30%.
Source zone pore volume (L)	407,808		407,808	
Target injection volume (L)	203,904	Targets 50% of the pore volume.	203,904	Targets 50% of the pore volume.
Target concentration of injectate	3 g/L	Keep below nBA solubility (same as DEM/VAL)	1%	Typical oil concentration (from EVO) for source areas.
Target mass of donor into formation (kg)	620		1880	
Resulting safety factor	7	Target mass into formation/stoichiometric donor demand	29	Target mass into formation/stoichiometric donor demand
Injection points	40	Direct push on 10 ft centers (assumes 5 ft radius)	40	Direct push on 10 ft centers (assumes 5 ft radius)
NAPL dissolution enhancement	1.5	PED versus EVO	1	
Treatment time (years)	6.7	Assumed treatment will be 50% faster than EVO due to dissolution enhancement	10	Assumed 10 years of treatment
Treatment frequency	4 applications	Applied more frequently than EVO (every 2 years) because less TOC mass is applied in each application.	4 applications	Every 2.5 years
Total donor mass to inject (kg)	2500		7600	

Notes: Treatment applications are fixed to four for each technology. Treatment time is variable.

 $ft^3 = cubic feet$

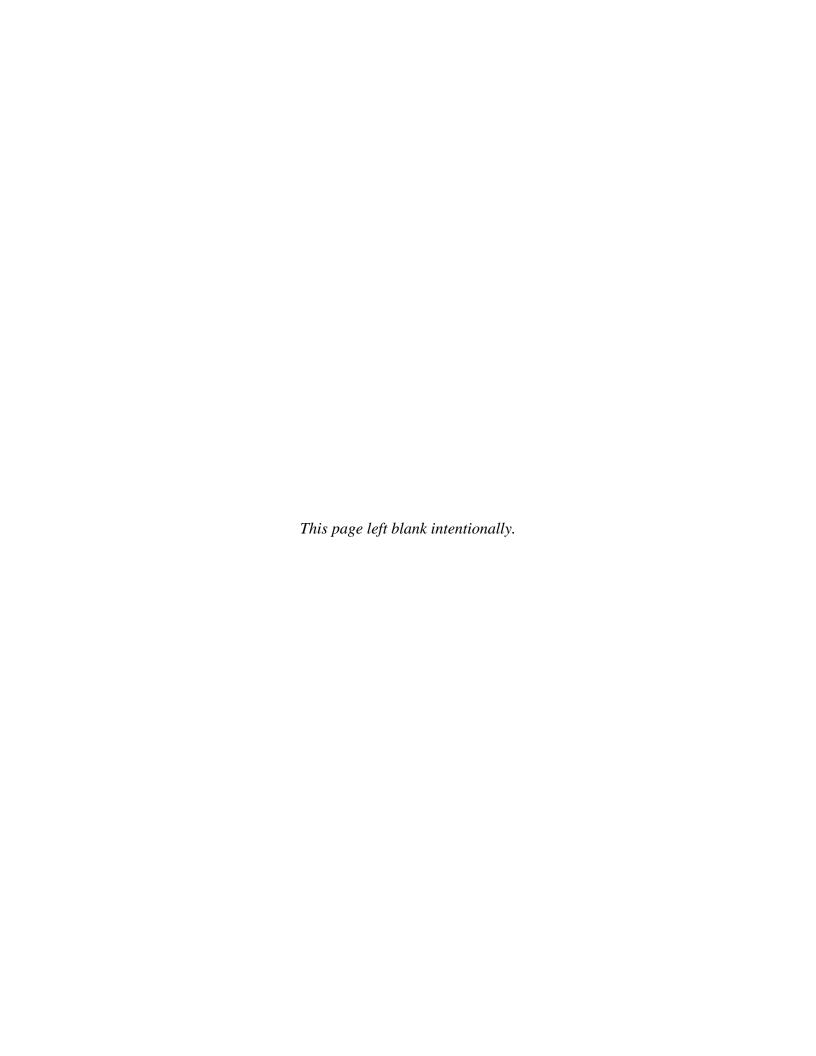
L = liter

Table 5 shows the total estimated treatment costs for the two scenarios – PED versus EVO. The calculated costs assume that the DNAPL and Site were previously well characterized. The total cost using PED as the electron donor is estimated to be \$571,000, while the total cost using EVO is estimated to be \$679,000. The differences in overall cost are attributable to the cost of donor applied in each event (which is a function of the unit cost and amount of donor required; the estimated number of applications is the same in both cases) and the duration of the remedy, which governs the number of monitoring events. Since other costs are likely to be similar between the two technologies, the cost savings with the PED technology arises primarily from the reduced duration of the remedy. The shorter duration is directly related to the enhanced DNAPL dissolution promoted by the PED.

The PED technology is applicable to the majority of sites with DNAPL source zones. Acceptance of the technology may significantly reduce remediation costs. The PED technology may also alleviate the drive to use other more aggressive and costly technologies to treat source zones, for example, thermal and chemical oxidation. Although the cost analysis presented here considered direct injection, groundwater recirculation systems could also be used. Existing pump and treat systems could benefit from introducing PED to create a small biological degradation/containment zone in and around the source area. This would eliminate or significantly reduce the amount of groundwater extraction (and associated costs) required to maintain containment while reducing the overall treatment time.

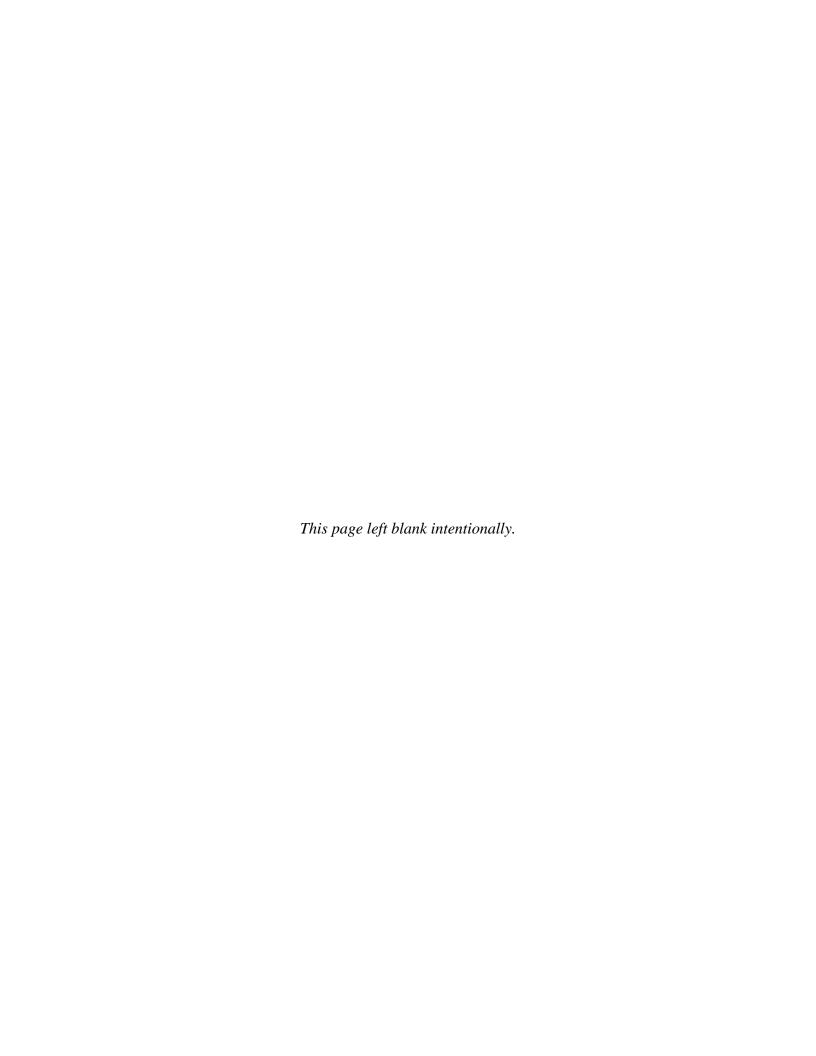
Table 5. Cost comparison of PED technology to EISB using conventional donor (EVO). Hot Spot 1, LC34, CCAFS/ESTCP Project ER-200716.

		PED		EVO			
Cost Element	Unit	Unit Cost (\$)	No.	Cost (\$)	Unit Cost (\$)	No.	Cost
Bench Scale Treatability Study	LS	20,000	1	20,000	20,000	1	20,000
Monitoring Well Installation	LS	20,000	1	20,000	20,000	1	20,000
Drilling Subcontractor	well	2500	5	12,500	2500	5	12,500
Well Development	well	500	5	2500	500	5	2500
Oversight	hr	100	50	5000	100	50	5000
Donor Application	Event	94,750	4	379,000	107,687	4	460,748
Donor	kg	7.50	620	4650	4.30	4090	17,587
Bioaugmentation Culture	L	255	20	5100	255	20	5100
DPT Subcontractor	LS	75,000	1	75,000	75,000	1	75,000
Oversight	hr	100	100	10,000	100	100	10,000
Groundwater Monitoring	Event	9475	16	151,600	9475	22	208,450
Analytical	LS	1875	1	1875	1875	1	1875
Sampling Equipment	LS	200	1	200	200	1	200
Sampling Labor	hr	100	24	2400	100	24	2400
Reporting	LS	5000	1	5000	5000	1	5000
Total				\$570,600			\$679,198



8.0 IMPLEMENTATION ISSUES

This DEM/VAL confirmed that nBA can be a suitable option for source treatment. Application of the nBA used conventional direct push tooling equipment. No special equipment was required and injection used standard commercial off-the-shelf materials. It should be noted that the PED, n butyl acetate, is a Class 1B flammable liquid. It is a colorless liquid that volatilizes to form dense vapors which have the potential to form an explosive mixture with air. Handling precautions such as bonding and grounding are required when working with the pure phase nBA. In addition, nBA is known to harm some plastics, such as those composed of polyvinyl chloride (PVC). Care must be taken to ensure that nBA is adequately dissolved if it is applied near PVC wells.



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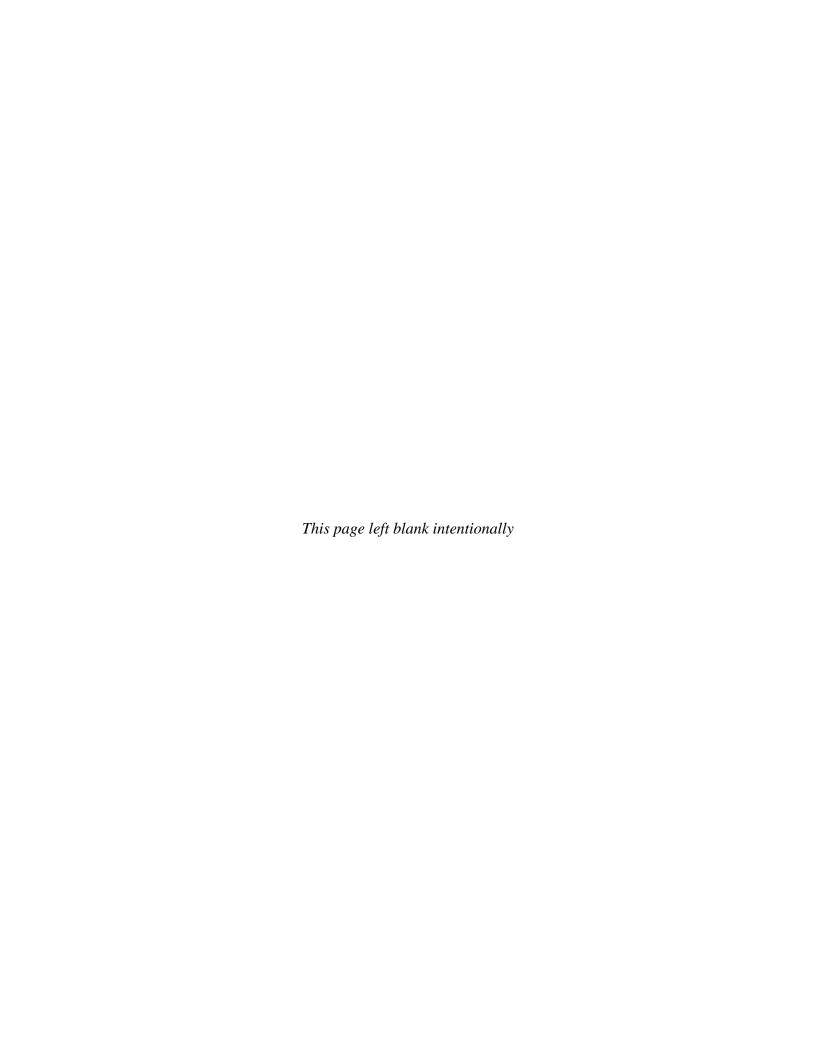
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